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## Antioxidant effectiveness of vitamin E in HDPE and tetradecane at 32°C

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### Abstract

Vitamin E was found to be a very effective antioxidant both in a model, liquid alkane, (tetradecane) and in HDPE when oxidations at close to room temperature were initiated with  $\gamma$ -radiation. FTIR was used to follow changes in vitamin E in oxidising tetradecane and HDPE, even at very low concentrations of the antioxidant. Formation of isolated hydroperoxide groups as a direct result of the vitamin E–peroxyl radical reaction were clearly visible. Quinone products from vitamin E were formed during  $\gamma$ -irradiation, but different quinones were formed depending on the vitamin E concentrations. Vitamin E quite effectively retarded the oxidation of HDPE during  $\gamma$ -irradiation and so should be useful in polyethylene intended for radiation sterilisation, as packaging materials or medical devices. Crown copyright © 2001 Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* HDPE oxidation; Tetradecane oxidation; Vitamin E antioxidant; Gamma initiation

### 1. Introduction

Antioxidant effectiveness in polyolefins, such as high density polyethylene (HDPE), has been studied for many years [1,2]. These studies on the solid polymers have been largely focussed on the technically important comparison of overall effectiveness by, for example, suppressing the accumulation of total carbonyl species in HDPE and changes in physical properties. The actual chemical changes in the host polymer and especially the antioxidant additives themselves are less well documented. These latter changes have been examined in detail in model, liquid systems, where the analytical problems are more tractable, and inferred to be similar in solid polymers at modest temperatures [1–3]. In addition, studies of the thermal oxidation of polyolefins have largely employed temperatures at or above 120°C in order to give acceptably short, accelerated test periods [1,4,5]. However, for many applications such as packaging of foodstuffs and medical devices, there is

interest in the performance of antioxidants in plastics over long periods, at temperatures close to ambient.

Some important information on antioxidant reactions and products in polymers can be obtained from analyses on liquid extracts from the solid polymer. However, these analyses are often complex. Also extraction may be far from quantitative, insensitive to products that become grafted to the polymer and may lead to changes in the additive or its conversion products as a result of extraction conditions [6–9]. Direct analyses on the solid polymer by spectroscopic techniques such as Fourier transform infrared (FTIR), coupled with spectral subtraction, and electron paramagnetic resonance (EPR) can overcome these drawbacks [1,9,10].

In this work, we have used FTIR to examine the reactions that occur during the  $\gamma$ -initiated oxidation of HDPE and a model *n*-alkane (tetradecane), both with and without the antioxidant vitamin E ( $\alpha$ -tocopherol). To our knowledge, no studies exist on the effectiveness of vitamin E in the stabilisation of HDPE during oxidation at close to room temperature. In addition,  $\gamma$ -initiation provides a particularly convenient method to initiate polymer oxidation without the complication of initiation by impurities of unknown composition and concentration, as is usually the case for thermal and photo-initiated processes in HDPE.

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## 2. Experimental

The *n*-alkane tetradecane [ $\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$ ] was purchased from Aldrich Chemicals. Two HDPE formulations used in this study were prepared by Pétromont (Varenes, Quebec). They included HDPE pellets melt compounded with 0.016 and 0.1 wt.% vitamin E [ $\alpha$ -tocopherol or 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)-2H-1-benzopyran-6-ol, Ciba Specialty Chemicals' Irganox E201 (92% in vitamin E)]. One formulation (0.016 wt.% vitamin E) was blow-moulded into beverage bottles with a wall thickness of 1000–850  $\mu\text{m}$ . Pellets of the 0.1 wt.% vitamin E sample were cold pressed into small discs of  $\sim 900$   $\mu\text{m}$  thickness. The crystallinity of all samples by differential scanning calorimetry (DSC) was 62% (heating rate  $10^\circ\text{C}/\text{min}$ , from 0 to  $250^\circ\text{C}$ , enthalpy of fusion of 100% crystalline HDPE assumed to be 280 J/g [11]). A 97% purity vitamin E sample from Aldrich Chemicals was also used in some of our work, together with a high purity sample prepared by column chromatography of vitamin E acetate, followed by de-acetylation. All three vitamin E samples were identical by infrared analysis. In the HDPE sample with 0.016 wt.% vitamin E, FTIR spectral subtraction (see below) indicated the presence of  $\sim 0.006$  wt.% of Tris(2,4-di-*tert*.butyl) phosphate, the conversion product from Tris(2,4-di-*tert*.butyl) phosphite, a commonly used, peroxide-decomposing, secondary antioxidant [9]. This phosphate concentration did not change significantly during our  $\gamma$ -irradiation experiments, although small amounts of 1,3-di-*tert*.butylbenzene were detected in the volatiles from both of the irradiated, Pétromont HDPE samples, containing 0.016 and 0.1% vitamin E. This product is an established radiolysis product from both the phosphate and phosphite [12].

For comparison purposes, samples with higher concentrations of vitamin E were prepared. First commercial HDPE/vitamin E samples cut from bottles were Soxhlet extracted for 64 h in dichloromethane to remove all additives. The samples were then immersed in a dichloromethane solution of vitamin E ( $\sim 2$  wt.%, Aldrich Chemicals, 97% purity) in a closed flask. The vitamin E was allowed to diffuse into the sample in the dark at  $35^\circ\text{C}$  for various times, up to a maximum of three weeks. After impregnation, the HDPE samples were briefly rinsed with dichloromethane and dried in vacuo for one week. The measured vitamin E concentrations in these samples ranged from 0.1 to 0.18 wt.%, depending on diffusion conditions. When these samples were treated with our SFE conditions, vitamin E was not extracted and, therefore, it can be assumed that the additive was not simply concentrated in the surface layers.

Antioxidant-free, HDPE samples of very similar morphology are required as references for very precise

spectral subtraction and for control samples in oxidation reactions. These samples were prepared from stabilised samples by Soxhlet extraction for 64 h with dichloromethane (Sigma-Aldrich). Although dichloromethane is very effective in removing antioxidants, it itself becomes entrapped in the extracted HDPE and impossible to remove completely, even by prolonged high vacuum at room temperature. Supercritical fluid extraction (SFE, ISCO SFX<sup>®</sup> 2-10 supercritical fluid extractor and ISCO 260D syringe pump), with carbon dioxide was used to remove this residual solvent from the HDPE samples after Soxhlet extraction and vacuum drying. SFE conditions were: temperature  $50^\circ\text{C}$ , pressure 400 atm, a time of 20 min in the static mode followed by 30 min in the dynamic mode at 5 ml/min flow rate. This procedure gave "clean" HDPE samples, that is free of additives and solvent residues, but with the same morphology as the initial HDPE/antioxidant samples as shown by infrared spectral subtractions. Unchanged morphology was found to be essential for meaningful subtraction of infrared spectra at high amplifications. Temperatures higher than  $50^\circ\text{C}$  in SFE were deliberately avoided to prevent morphological changes. A second cycle of Soxhlet extraction and SFE caused no further change in the IR of the HDPE, consistent with complete extraction of the antioxidants (AO) in the first cycle. When our mild conditions were used for direct SFE of antioxidants from HDPE/antioxidant samples, without a prior dichloromethane extraction, additives were not completely removed.

A Nordion Gammacell 220 with a  $^{60}\text{Co}$  source and a dose rate of 1.25 kGy/h (i.e. 0.125 Mrad/h) was used for  $\gamma$ -irradiation. All samples were  $\gamma$ -irradiated in static air at the ambient temperature in the Gammacell ( $\sim 32^\circ\text{C}$ ). Because of continued, post-irradiation oxidation, all samples were analysed within 30 min of the end of each  $\gamma$ -irradiation period.

Infrared analyses were carried out on a Midac M FTIR spectrometer (resolution  $4\text{ cm}^{-1}$ , 100 scans summation, DTGS detector, GRAMS/32 software). Because the IR signal at high expansion was found to be dependent on the morphology of the analysed portion of the sample ( $\sim 1.5 \times 1.5$  mm), metal holders that fitted directly into the FTIR were fabricated to allow  $\gamma$ -irradiation or thermal oxidation followed by FTIR analysis without sample demounting. This gave a self-consistent series of analyses on exactly the same sample area. To allow identification and quantification of overlapped carbonyl absorption, some oxidised tetradecane and HDPE samples were treated with gaseous sulphur tetrafluoride ( $\text{SF}_4$ ). This reagent can diffuse through the polymer and convert carboxylic acid groups to acid fluorides, absorbing at  $\sim 1845\text{ cm}^{-1}$  [13]. This latter absorption is completely separated from the carbonyl region, which in turn is simplified by removal of the acid absorption. In addition, all alcohol and hydroperoxide

groups become simple fluorides, removing hydrogen bonding interactions which broaden the carbonyl absorptions. For our  $\sim 850 \mu\text{m}$  samples,  $\text{SF}_4$  treatment for  $\sim 72$  h was required for a complete reaction.

### 3. Results

To estimate vitamin E concentrations in the Pétromont HDPE samples (both blown bottles and HDPE impregnated in the laboratory), solutions of vitamin E (97% purity), were prepared in tetradecane. Concentrations in HDPE were estimated from their IR spectra, assuming that molar extinction coefficients ( $\epsilon$ ) were identical in HDPE and in the alkane. Even in environments as similar as tetradecane and HDPE, there are small shifts in the peak maxima for the phenolic O–H bands of vitamin E,  $3636 \text{ cm}^{-1}$  in tetradecane and  $3631 \text{ cm}^{-1}$  in HDPE. Concentrations are listed in Table 1.

#### 3.1. Study of $\gamma$ -irradiated, tetradecane and its vitamin E solutions

Vitamin E was irradiated in the liquid *n*-alkane to help with the subsequent identification of changes in HDPE. Liquid *n*-alkanes are obviously free of morphology-related IR bands, both before and after irradiation. This allows extremely precise spectral subtraction at an order of magnitude greater sensitivity than practicable in semi-crystalline HDPE. The antioxidant effects of vitamin E on the oxidation of a linear, liquid alkane were investigated by observing oxidation products in  $\gamma$ -irradiated solutions of vitamin E in tetradecane. Four solutions were analysed by FTIR spectroscopy before and after irradiation (Table 1). The  $\gamma$ -irradiation of pure tetradecane leads to an increase in

IR bands from many, well characterised oxidation products: ketone at  $1722 \text{ cm}^{-1}$  (Fig. 1A, extinction coefficient,  $\epsilon$ ,  $350 \text{ kg/mol/cm}$ ) and –OH species (not shown, but generally similar to those found in HDPE, below), including free (non-hydrogen bonded) hydroperoxide at  $3557 \text{ cm}^{-1}$  ( $\epsilon$   $90 \text{ kg/mol/cm}$ ), free alcohol at  $3626 \text{ cm}^{-1}$  ( $\epsilon$   $90 \text{ kg/mol/cm}$ ), hydrogen-bonded hydroxyl (alcohol and hydroperoxide) at  $\sim 3430 \text{ cm}^{-1}$  ( $\epsilon$   $90 \text{ kg/mol/cm}$ ), [13,14]. For the solutions with vitamin E, the ketone absorption is slightly shifted to  $1718 \text{ cm}^{-1}$  and some new, additional bands attributed to quinones are observed in the carbonyl region at  $1684$ ,  $1655$ ,  $1645$  and  $1598 \text{ cm}^{-1}$  (Fig. 1, B and C) [14]. The  $1645 \text{ cm}^{-1}$  peak could be partly attributed to growth of polymer unsaturation. However, although a slight increase in the trans-vinylene absorption at  $966 \text{ cm}^{-1}$  was seen, this was insignificant compared with the  $1645 \text{ cm}^{-1}$  growth in irradiated, vitamin E stabilised tetradecane. Furthermore, there is no visible increase at  $1645 \text{ cm}^{-1}$  in pure tetradecane (Fig. 1A).  $\text{SF}_4$  treatment of tetradecane after  $\gamma$ -irradiation caused the clear growth of an  $1845 \text{ cm}^{-1}$  IR absorption (not shown), attributed to an acid fluoride ( $\epsilon$   $650 \text{ kg/mol/cm}$ ), [13]. The acid to ketone molar ratio was found to be 1:6 for both stabilised and non-stabilised tetradecane. IR changes resulting from  $\text{SF}_4$  treatments are discussed in detail in the HDPE Section 3.2.

Kinetic changes in irradiated tetradecane, both with and without vitamin E, are collected in Fig. 2. For the 0.016 wt.% vitamin E solution, its oxidation behaviour differs in only a minor way from pure tetradecane (Fig. 2A) and its product changes are not shown. Loss of the phenolic function of vitamin E was also calculated from the decrease in its  $1209 \text{ cm}^{-1}$  absorption (phenolic C–OH). These values were very close to those shown in Fig. 2 (B and C). From the IR study

Table 1  
Initial concentrations and rates of conversion during  $\gamma$ -initiated oxidation

Antioxidant type	Initial antioxidant concentration, mol. equiv. phenol/l (wt.%)	-d[Phenol]/dt, equiv/l kGy	Initial d[free ROOH]/dt, mol/l kGy	Initial d[ketone]/dt, mol/l kGy	Final <sup>a</sup> d[ketone]/dt, mol/l kGy
<i><math>\gamma</math>-Initiated oxidation of tetradecane<sup>b</sup></i>					
None	0	–	$0.7 \times 10^{-4}$	$1.8 \times 10^{-4}$	$1.8 \times 10^{-4}$
Vit E	$2.7 \times 10^{-4}$ (0.016)	$2.3 \times 10^{-4}$	$2.7 \times 10^{-4}$	$0.32 \times 10^{-4}$	$1.8 \times 10^{-4}$
Vit E	$1.8 \times 10^{-3}$ (0.1)	$2.7 \times 10^{-4}$	$3.4 \times 10^{-4}$	$0.24 \times 10^{-4}$	$1.9 \times 10^{-4}$
Vit E	$3.5 \times 10^{-2}$ (2.0)	$3.1 \times 10^{-4}$	$2.7 \times 10^{-4}$	$0.17 \times 10^{-4}$	ND <sup>c</sup>
<i><math>\gamma</math>-Initiated oxidation of HDPE<sup>b</sup></i>					
None	0	–	$0.7 \times 10^{-4}$	$2.1 \times 10^{-4}$	$1.5 \times 10^{-4}$
Vit E	$3.6 \times 10^{-4}$ (0.016)	$1.4 \times 10^{-4}$	$1.9 \times 10^{-4}$	$1.1 \times 10^{-4}$	$1.5 \times 10^{-4}$
Vit E	$2.3 \times 10^{-3}$ (0.10)	$1.9 \times 10^{-4}$	$1.7 \times 10^{-4}$	$0.64 \times 10^{-4}$	$1.5 \times 10^{-4}$
Vit E	$4.2 \times 10^{-3}$ (0.18)	$2.2 \times 10^{-4}$	$1.8 \times 10^{-4}$	$0.091 \times 10^{-4}$	$1.4 \times 10^{-4}$

<sup>a</sup> Rate after complete destruction of the phenolic function of vitamin E.

<sup>b</sup> After  $\gamma$ -irradiation in air at  $32^\circ\text{C}$ .

<sup>c</sup> Not determined.

of the  $\gamma$ -initiated oxidation of tetradecane, the initial and final rates of formation of ketones, free (non-hydrogen bonded) secondary hydroperoxide and vitamin E loss are collected in Table 1 for all three vitamin E concentrations studied and for pure tetradecane. The “final” rates of ketone formation (after complete loss of the phenolic OH) are also shown in Table 1.

### 3.2. Study of $\gamma$ -irradiation of HDPE, stabilised with phenolic AOs

Four HDPE samples (clean, i.e. exhaustively extracted, and with 0.016, 0.1 and 0.18 wt.% of vitamin E) were  $\gamma$ -irradiated and the changes in the hydroxyl and carbonyl absorption regions followed by infrared spectroscopy (Fig. 3). For the samples with vitamin E, visible decreases in the phenolic –OH band (at  $3635\text{ cm}^{-1}$ ) were observed, together with some increases near  $1680\text{ cm}^{-1}$ , consistent with the formation of quinones. For all HDPE samples, their  $\gamma$ -oxidation is characterised by formation of free hydroperoxides at  $3550\text{ cm}^{-1}$ , free alcohols at  $3625\text{ cm}^{-1}$ , bonded alcohols and hydroperoxides from  $3600$  to  $3200\text{ cm}^{-1}$ , carbonyl (strongly overlapped ketones and carboxylic acids) at  $1718\text{ cm}^{-1}$ ,  $\gamma$ -lactones at  $1770\text{ cm}^{-1}$  and *trans*-vinylene bonds at  $966\text{ cm}^{-1}$  [1,10,13]. Kinetic changes for key groups are shown in Fig. 4.

The rate of *trans*-vinylene formation in HDPE was found to be almost double that found in tetradecane. In

parallel, there is a decrease in the initial vinyl bands at  $908$ ,  $991$  and  $1645\text{ cm}^{-1}$  [13]. These initial, unsaturation bands are probably related to the catalysis system used in HDPE synthesis. Vinyl loss may result from facile addition of radicals during  $\gamma$ -irradiation, or from the ease of abstraction by peroxy radicals of allylic hydrogens as compared to alkyl hydrogens during oxidation [15].

Compared to tetradecane (Fig. 1A),  $\gamma$ -irradiation of “clean” HDPE leads to a broader carbonyl band centred at  $\sim 1717\text{ cm}^{-1}$ . This broadening may be attributable to hydrogen bonding in the locally oxidised domains and to increased carboxylic acid formation. This was confirmed by  $\text{SF}_4$  treatment of the  $\gamma$ -irradiated HDPE samples. The  $\sim 1717\text{ cm}^{-1}$  absorption sharpened and moved to  $1719\text{ cm}^{-1}$  as all –OH groups are destroyed and as carboxylic acid was converted to acid fluoride with a sharp peak at  $1846\text{ cm}^{-1}$  (Fig. 5). Based on extinction coefficients for acid fluoride of  $\sim 650\text{ kg/mol/cm}$  (at  $1845\text{ cm}^{-1}$ ) and for ketone of  $\sim 350\text{ kg/mol/cm}$  (at  $\sim 1719\text{ cm}^{-1}$ ), after  $\gamma$ -irradiation the carboxylic acid concentration was found to be 1/2 of the ketone level for both stabilised and non-stabilised HDPE. Similar proportions were found in stabiliser-free HDPE in previous studies [13]. A time of 18 h was chosen for irradiation so as to ensure the presence of some vitamin E throughout the reaction (cf. Fig. 4B). During the oxidation that continues after irradiation, the acid to ketone ratio was found to dwindle towards zero [16]. The  $\text{SF}_4$

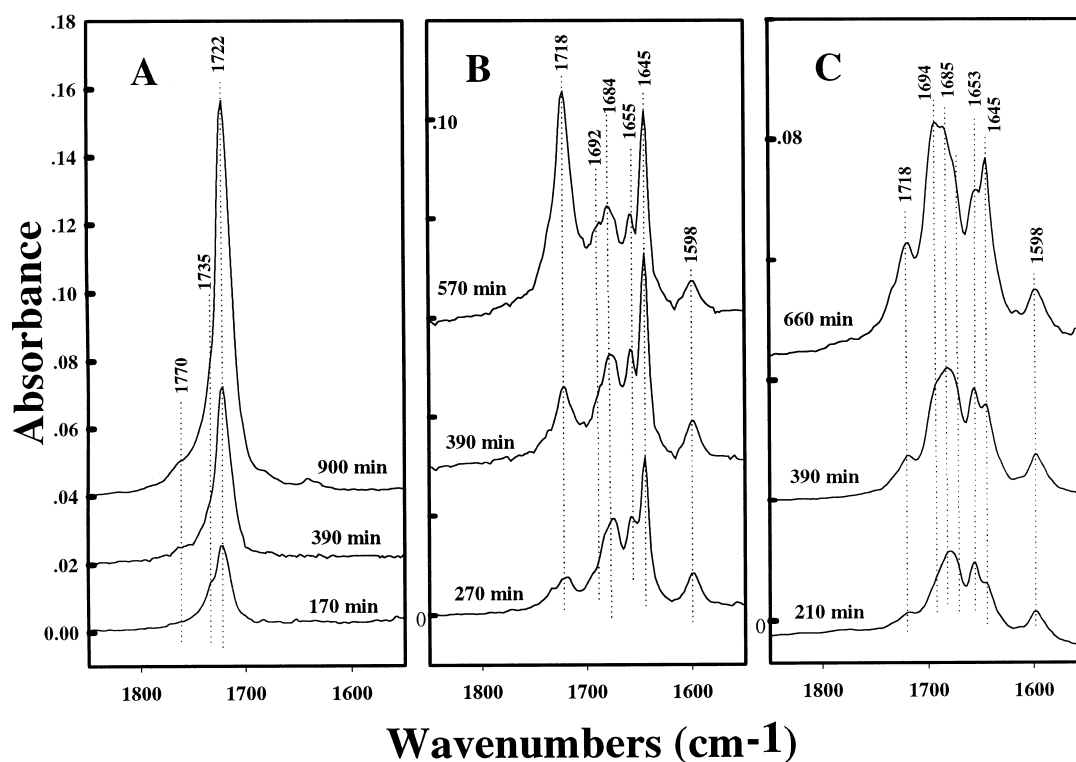


Fig. 1. Evolution of infrared spectra in carbonyl region for  $\gamma$ -irradiated, tetradecane solutions: 1.0 mm path, NaCl IR cell. Note differences in the absorbance scales. (A) pure tetradecane; (B) 0.1 wt.% vitamin E in tetradecane; (C) 2 wt.% vitamin E in tetradecane.

treatment of the  $\gamma$ -irradiated, vitamin E containing samples of HDPE appears to be complicated by some loss of quinone products, especially at  $\sim 1645\text{ cm}^{-1}$  (Fig. 5). This peak is clearly visible in the lower vitamin E containing tetradecane solution upon irradiation (Fig. 1B). In addition this quinone peak is strongly overlapped with the negative peak, resulting from vinyl group loss (also at  $1645\text{ cm}^{-1}$ ).

The “final” rates of ketone formation (after complete loss of the phenolic–OH) are also shown in Table 1.

For low vitamin E concentrations in HDPE, the true decreases in the phenolic–OH band at  $3631\text{ cm}^{-1}$  of

vitamin E were complicated by the concomitant growth in the free alcohol absorption at  $3625\text{ cm}^{-1}$  as oxidation proceeds. Hence another IR band for the determination of the decrease in the phenolic antioxidant was sought. From studies on  $\gamma$ -irradiated, tetradecane solutions of vitamin E, the decrease of the phenolic–OH band was found to be accompanied by a decrease in its  $1209\text{ cm}^{-1}$  band (presumed to be the phenol C–OH absorption [14],  $\epsilon$  calculated to be  $200\text{ kg/mol.cm}$ ). In contrast to the phenol O–H absorption, this sharp IR band is not overlapped with bands from the oxidation products of the alkane or HDPE. Fig. 4B shows the changes in

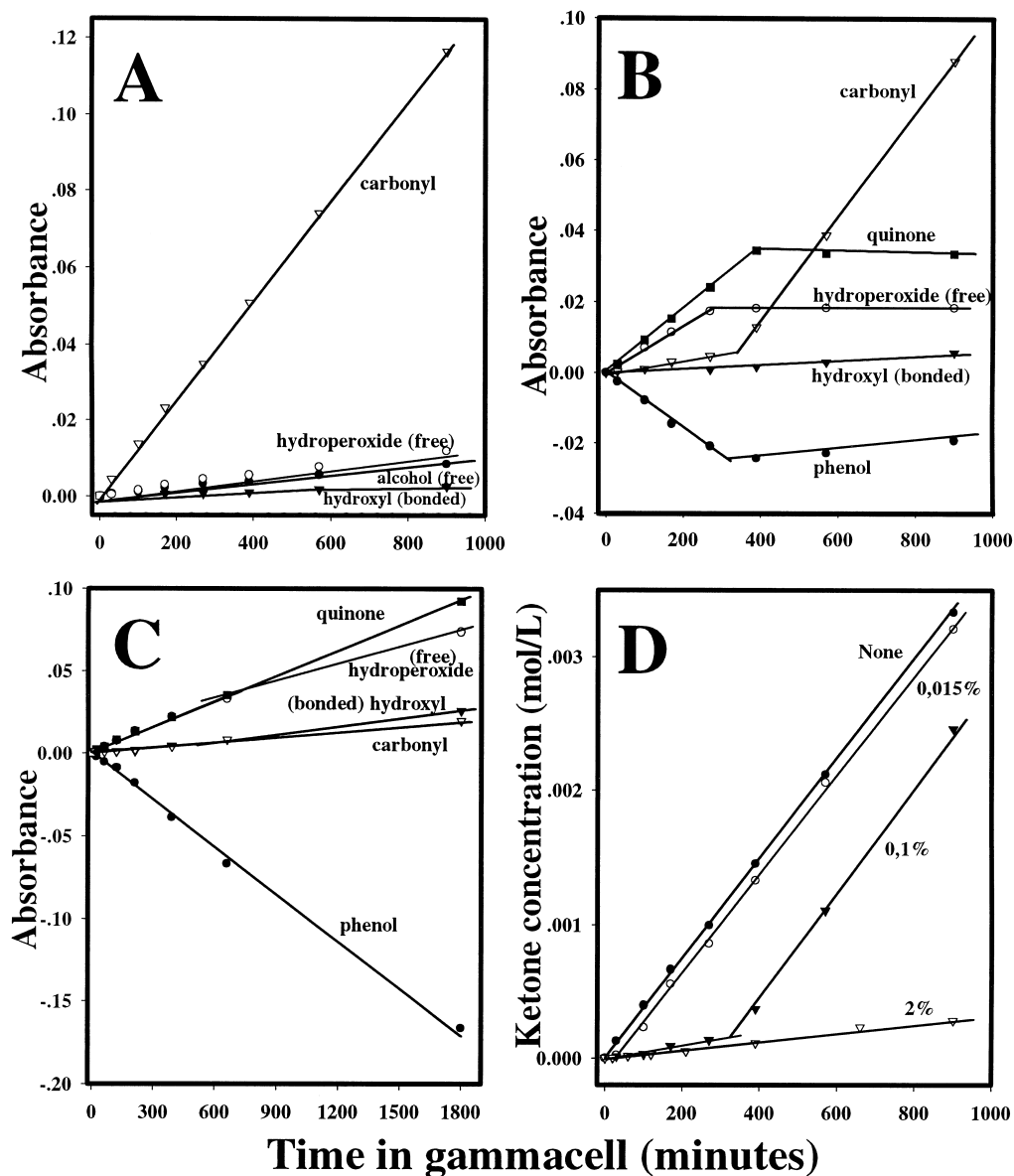


Fig. 2. Tetradecane  $\gamma$ -initiated oxidations: changes in infrared absorptions and concentrations of various oxidation products. All spectra were measured in 1.0 mm path, NaCl IR cells. (A): pure tetradecane; (B): 0.1 wt.% vitamin E in tetradecane; (C): 2 wt.% vitamin E in tetradecane. Concentrations were calculated from IR bands at  $1722\text{ cm}^{-1}$  (carbonyl),  $3627\text{ cm}^{-1}$  (free alcohol),  $3550\text{ cm}^{-1}$  (free hydroperoxide),  $3430\text{ cm}^{-1}$  (bonded alcohol and hydroperoxide),  $3635\text{ cm}^{-1}$  (phenol O–H) and  $1645\text{ cm}^{-1}$  (quinone). (D): formation of ketone in the four solutions studied (pure tetradecane and 0.015, 0.1 and 2 wt.% of vitamin E in tetradecane).

phenol group concentration derived from both vitamin E bands during  $\gamma$ -irradiation. These IR changes were found to give similar phenol concentration changes. Furthermore, phenol loss has been confirmed on polymer extracts by liquid chromatography [9].

The initial rates of formation of ketone and free hydroperoxide groups, together with loss of the phenolic function of vitamin E and “final” rates of ketone formation in HDPE samples are collected in Table 1 and plotted in Fig. 6.

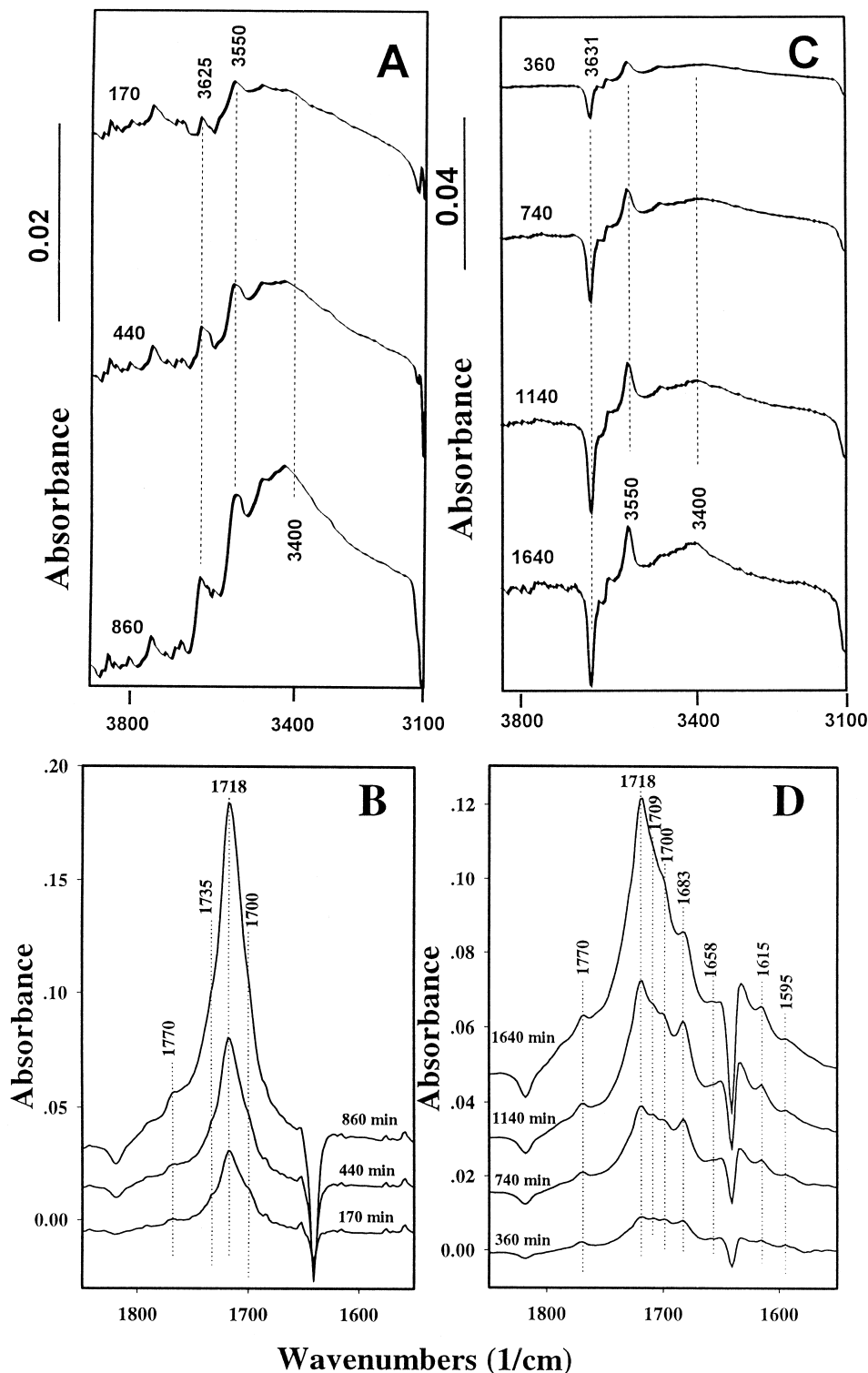


Fig. 3. Evolution of infrared spectra in hydroxyl and carbonyl regions during  $\gamma$ -irradiation of HDPE. (A) and (B): antioxidant free HDPE. (C) and (D) HDPE with 0.185 wt.% of vitamin E. Times refer to  $\gamma$ -irradiation periods. Note differences in the absorbance scales.

#### 4. Discussion

Vitamin E is a very powerful antioxidant in nature [17–19]. For a decade its activity has been extensively studied in the liquid phase [20]. Vitamin E in fatty foods has been reported to be very rapidly destroyed by  $\gamma$ -irradiation, presumably because of its antioxidant function (see below) [21].

Vitamin E has been used as an efficient melt flow stabiliser in [4,7,22]. Also it has shown potential for the reduction of off-flavours related to polymer oxidation during processing [22]. Recently vitamin E has also

been found to prevent fatigue cracks in UHMWPE for medical implants [23]. Vitamin E activity at  $> 120^\circ\text{C}$  in oxidising polypropylene was found to be very effective, but less so than some other industrial phenols [4,5]. These same articles pointed out that the accelerated test conditions were unrealistically high for many applications. The changes in Figs. 2 and 4 clearly confirm the action of vitamin E as an effective antioxidant in liquid tetradecane and in solid HDPE. Phenolic antioxidants can retard the oxidation of  $\gamma$ -irradiated polymers, although in many cases at the expense of severe yellowing [24]. Some degradation products from phenolic

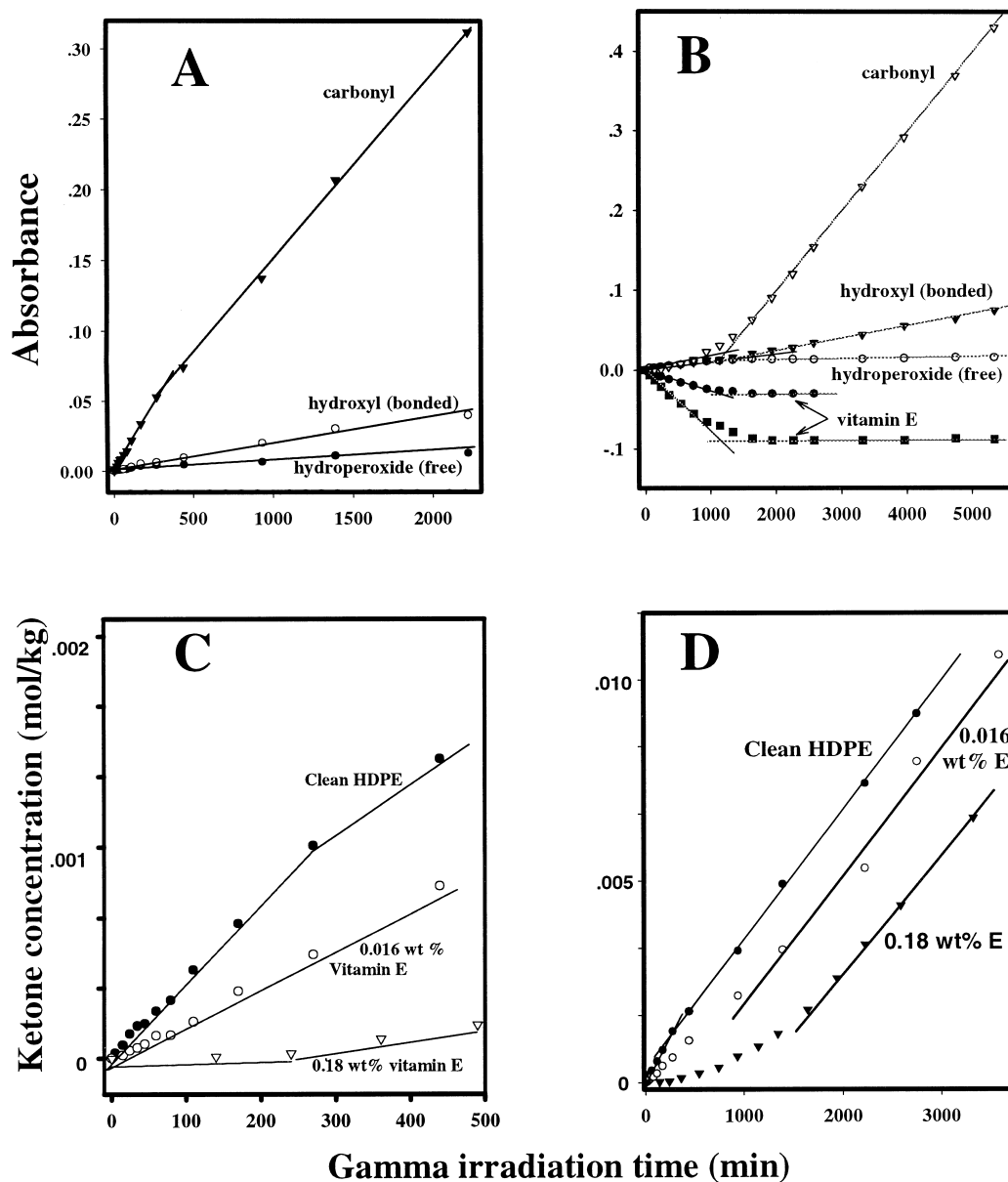


Fig. 4. HDPE  $\gamma$ -initiated oxidations: changes in infrared absorptions and concentrations of various oxidation products. From IR bands at  $1718\text{ cm}^{-1}$  (carbonyl),  $3550\text{ cm}^{-1}$  (free hydroperoxide),  $3420\text{ cm}^{-1}$  (bonded alcohol and hydroperoxide),  $3631\text{ cm}^{-1}$  (vitamin E's phenol O–H, upper curve in B) and  $1209\text{ cm}^{-1}$  (vitamin E's phenol C–OH, lower curve in B). All absorbances normalised to  $1000\text{ }\mu\text{m}$  sample thicknesses. (A) in antioxidant-free HDPE and (B) in 0.185 wt.% vitamin E in HDPE. (C) and (D) compare the formation rate of carbonyl compounds in three of the HDPE samples for (C) short and (D) longer,  $\gamma$ -irradiation times.



antioxidants have already been observed during irradiation [25,26].

For polymers such as polyethylene with quite simple IR spectra, transmission IR with spectral subtraction on

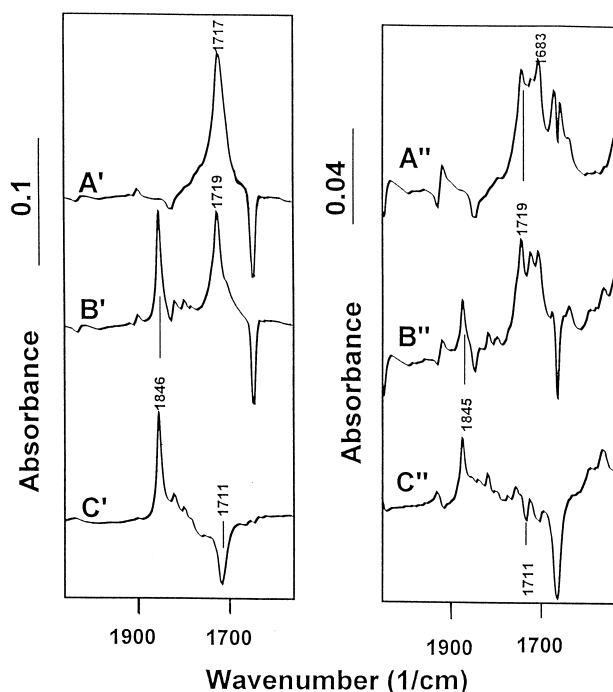


Fig. 5. Effects of  $\text{SF}_4$  treatment on 18 h,  $\gamma$ -irradiated HDPE samples. A: before  $\text{SF}_4$  treatment; B: after  $\text{SF}_4$  treatment; C: subtraction (after  $\text{SF}_4$ -before  $\text{SF}_4$ ). A', B' and C' for antioxidant-free HDPE. A'', B' and C'' for HDPE with 0.18 wt.% of vitamin E.

thick samples is a direct, practical method to follow changes in both additives and in the solid polymer [1,9]. Additives and their conversion products can be studied directly in situ, without recourse to extraction. Extraction is often non-quantitative (for example, if grafting has occurred) and can cause changes in additives and products during the extraction process [6–9]. There is one major drawback to identification and quantification of changes in a semi-crystalline polymer from small bands by spectral subtraction. If the IR analyses are not made close to the same place in the sample, slight shifts in absorption maxima were found to occur (presumably because of small morphology differences), leading to subtraction artefacts, which may be interpreted as real absorptions. This was overcome by permanently mounting each sample in a rigid metal frame that fitted precisely into the FTIR spectrometer's sample holder. In addition, because HDPE possesses two weak bands at 3643 and 3604  $\text{cm}^{-1}$ , the phenolic O–H band of vitamin E (at 3631  $\text{cm}^{-1}$ ) is particularly difficult to quantify at low vitamin E concentrations. The true maximum of this band was, therefore, determined in the samples containing 0.1 and 0.18 wt.% of vitamin E. Quantification at lower levels was based upon changes in the C–OH band at 1209  $\text{cm}^{-1}$ .

In both liquid tetradecane and HDPE, it can be seen that  $\gamma$ -irradiation is an attractive method for oxidation initiation, because formation of oxidation products is very linear and because controlled oxidation can be triggered at ambient temperature (Figs. 2 and 4). Expo-

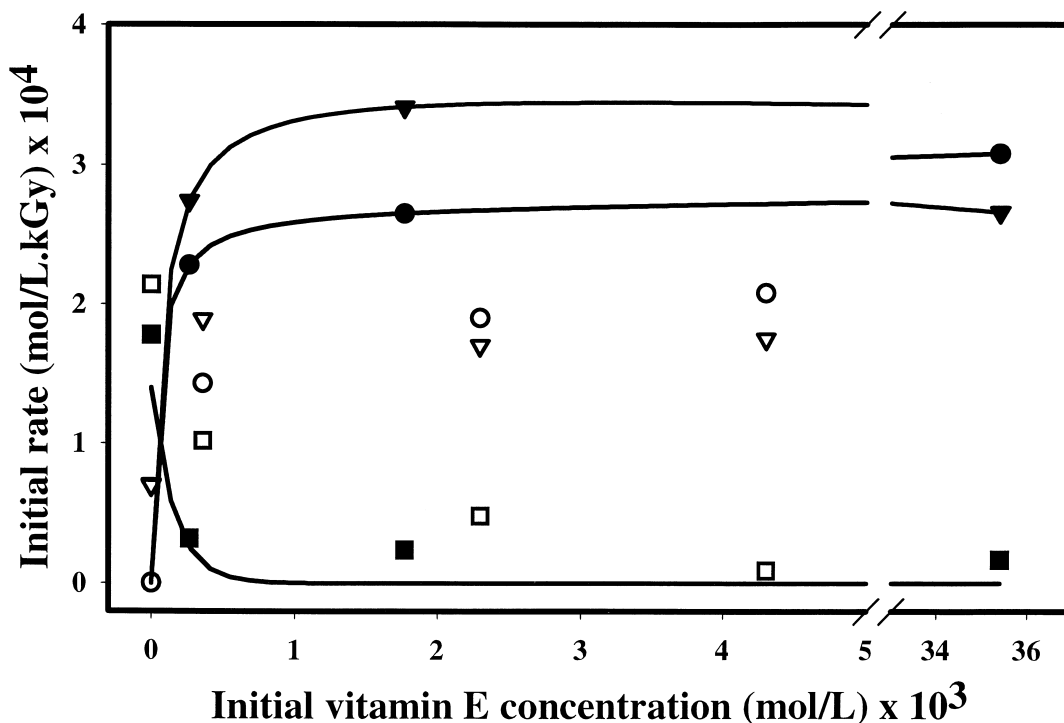
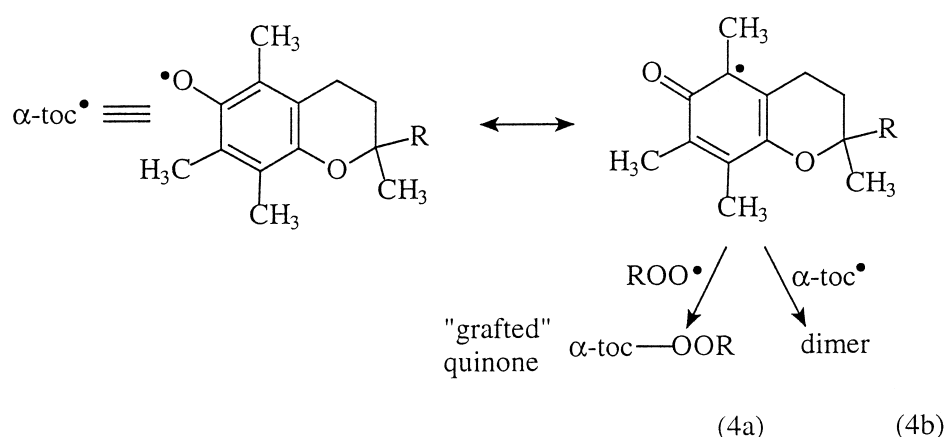
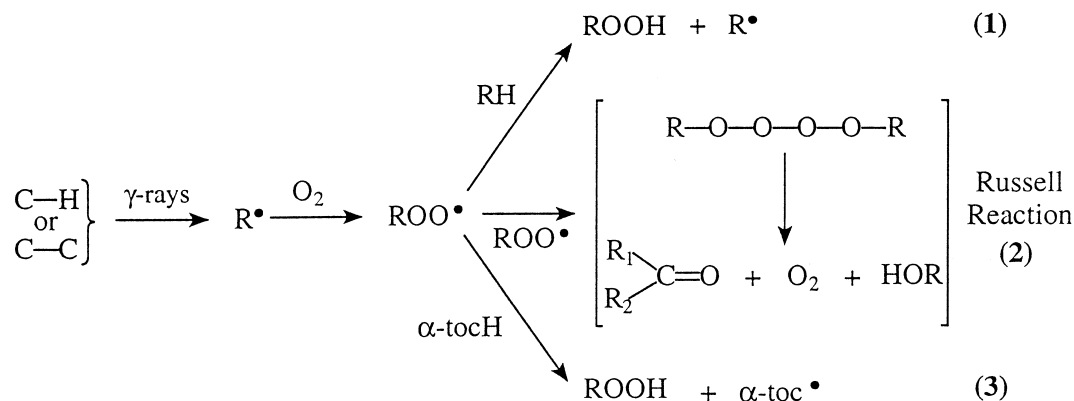
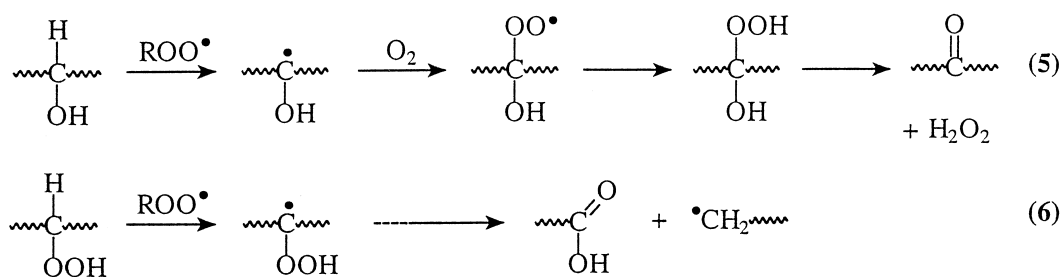


Fig. 6. Initial reaction rates in tetradecane and HDPE with several vitamin E concentrations. In tetradecane: ● vitamin E loss; ▼ free hydroperoxide formation; ■ ketone formation. In HDPE: ○ vitamin E loss; ▽ free hydroperoxide formation; □ ketone formation.



Scheme 1.



Scheme 2.

mental growth curves are the norm from photo- and thermally initiated oxidations of HDPE because of the instability of various oxidation products under these initiation conditions [13].

Scheme 1 shows the “classical” reactions generally assumed to occur in the oxidation of alkanes containing phenolic antioxidants. The  $\gamma$ -irradiation of both tetradecane and HDPE results in bond scission that leads to predominantly second alkyl radicals (G radical formation  $\sim 3$ , i.e.  $\sim 3 \times 10^{-4}$  mol/l kGy [27]). Most alkyl radicals undergo a very fast reaction with dissolved  $\text{O}_2$  to give peroxy radicals (G peroxy radical formation in HDPE  $\sim 2$ , i.e.  $\sim 2 \times 10^{-4}$  mol/l kGy) [28]. Each initial

peroxy radical may propagate by the abstraction of a hydrogen atom from the alkane to give hydroperoxide, reforming peroxy radicals [reaction (1)], or undergo cage termination with its geminate radical. Secondary peroxy radicals are expected to self-react by the Russell reaction (2) to give equivalent yields of ketones and sec. alcohols [29]. However, it has been previously reported that less sec. alcohol than ketone species is found in both oxidised liquid hydrocarbons and in  $\gamma$ -irradiated polyethylene [13,30]. This is clearly confirmed by our data (cf. Figs. 2 and 4). This lack of sec. alcohol products may result from their rapid, peroxy radical attack (Scheme 2) to yield ketonic groups [31]. Peroxy radical

attack in reaction (5) is reported to be over 100 times faster than radical attack in reaction (1) (Scheme 1) [32]. However, the low alcohol yields (as compared to ketone), even in the early stages of irradiation, implies the involvement of other effects, such as formation of clusters or spurs of peroxy radicals (i.e. not simply single, geminate pairs) [33]. Reaction (6) may explain the formation of carboxylic acids, based on reactivity of secondary C–H sites carrying hydroperoxide functions. This reaction is also  $\sim 100$  times faster than attack on a second C–H site [32]. The carboxylic acid to ketone molar ratio was much higher in both stabilised and unstabilised HDPE (ratio 1:2) than in tetradecane (ratio 1:6). This is again consistent with spur reactions being more important in the solid polymer, where rapid diffusive averaging cannot occur.

As with other phenols, vitamin E is expected to inhibit the propagation of peroxy radicals because of its easily abstractable, phenolic hydrogen [reaction (3)] to form phenoxyl radicals and (initially) free hydroperoxide groups. Each phenoxyl radical can react further with peroxy radicals [reaction (4)]. From Table 1, the data for  $\gamma$ -initiated oxidation of tetradecane, in the presence of vitamin E indicate that free hydroperoxide is produced at a higher initial rate ( $\sim 3 \times 10^{-4}$  mol/l kGy) than found in pure tetradecane ( $\sim 0.7 \times 10^{-4}$  mol/l kGy), consistent with peroxy scavenging by reaction (3). In fact the increased rate of initial, free hydroperoxide production in the presence of vitamin E ( $\sim 2.3 \times 10^{-4}$  mol/l kGy) is close to the rate of vitamin E loss ( $\sim 2.6 \times 10^{-4}$  mol/l kGy), consistent with the reported G values ( $2\text{--}3 \times 10^{-4}$ ) for peroxy production in liquid alkanes and in HDPE [28]. As oxidation proceeds, the free hydroperoxide yield drops below that of phenol loss, probably as a result of hydrogen bonding increasing to accumulated oxidation products. This will shift the  $\text{--OOH}$  peak to  $\sim 3400$   $\text{cm}^{-1}$ , as suggested by Gugumus [34]. The initial rate of ketone formation in tetradecane is reduced up to 10 fold by vitamin E (Table 1). As soon as the phenolic function of vitamin E has been totally destroyed (after about  $\sim 350$  min of  $\gamma$ -irradiation for the 0.1 wt.% vitamin E in tetradecane), rapid carbonyl formation begins whereas formation of free hydroperoxides at  $3556$   $\text{cm}^{-1}$  stops almost completely (Fig. 2C). Furthermore, several bands at 1684, 1678, 1655, 1645 and  $1598$   $\text{cm}^{-1}$  (Fig. 1B and C) are formed and attributed to different quinonoid products [7,14]. Their formation again stops after approximately 350 minutes (Fig. 2C). The quinones may consist of dimers or spirodimers [7,35]. The bands at 1655 and  $1598$   $\text{cm}^{-1}$  are consistent with the formation of a spirodimer in tetradecane, similar to that formed in melt processing of vitamin E stabilised HDPE [7]. At 2% vitamin E, inhibition was protracted so that the additive concentration never dropped to zero during the duration of our experiments (Fig. 2C) and the ketone formation rate never increased during irradiation up to 2000 min.

As the phenol reacts, there are some differences in band intensities of quinones between the 0.1 and the 2% solutions (cf. Fig. 1B and C), with formation of quinone products around  $1684$   $\text{cm}^{-1}$  being more important in the 2% vitamin E solution. It is known that higher concentrations of vitamin E lead to increased concentrations of  $\alpha$ -tocopherylquinone and the spirodimer [35].

In broad terms, Table 1 shows quite similar rate values in unstabilised tetradecane and HDPE for free hydroperoxide formation and ketone formation. For vitamin E stabilised HDPE, the rates of phenol loss and free hydroperoxide increase are both about 60% of the corresponding liquid phase rates. In contrast, initial ketone formation is  $\sim 2\text{--}3$  times greater in stabilised HDPE than in stabilised tetradecane at equivalent vitamin E concentrations. In both liquid and solid, the final ketone formation rate after antioxidant destruction are very similar ( $1.5\text{--}1.8 \times 10^{-4}$  mol/l kGy, Table 1).

The kinetic curves in Fig. 4 for the “clean” HDPE samples require some further comment. After the first  $\sim 300$  min of  $\gamma$ -irradiation, there is a small, but real, drop in oxidation rate, followed by a completely linear, but slightly slower, carbonyl formation rate. Initially, this can be attributed to reaction with radicals of the oxygen dissolved in the polymer until partial oxygen depletion occurs. This is consistent with the dissolved oxygen value found in the literature (110 ppm in amorphous PE [36]) and the crystallinity of our HDPE (62%) determined by DSC. After this  $\sim 300$  min period, the slightly slower, constant oxidation rate probably results from the equilibrium situation, where oxygen reaction rate with radicals is just compensated by the oxygen diffusion rate.

Although the phenolic groups disappear in less than  $\sim 200$  min in the 0.016 wt.% vitamin E sample, a low residual antioxidant activity persists up to  $\sim 1500$  min in HDPE, as shown by the change in slope in Fig. 4C. As phenoxyl radicals are assumed to react very quickly by reactions (3) and (4a), this protracted antioxidant effect might be attributable to some reaction of the quinone products. However, the effect may be less pronounced than that proposed for the melt stabilisation of HDPE by [37]. For longer irradiation times ( $> 2000$  min), the carbonyl formation rate is the same for all three samples (Fig. 4D and Table 1), showing that there is no residual antioxidant activity.

The formation of free hydroperoxides at  $3556$   $\text{cm}^{-1}$  is increased in the presence of vitamin E as compared to formation in pure tetradecane or HDPE. This is consistent with inhibition by reaction (3). However, there is still initial formation of detectable ketonic groups, especially in HDPE, even with the higher vitamin E concentration. (Figs. 2D and 4D). This shows that some peroxy radicals escape being scavenged by reaction with the phenol or its phenoxyl radical and still self react, possibly as transient caged pairs [38].

When the vitamin E concentration was increased from 0.1 to 2 wt.%, the initial rate of ketone formation in the  $\gamma$ -irradiated, tetradecane solution was again lowered, but only by 30% as compared to the 0.1 wt.% case, despite the vitamin E concentration being multiplied 20 fold (Fig. 6). Similarly the initial rates of loss of the phenol band and formation of free hydroperoxide only increased by about 25% as compared to the 0.1 wt.% vitamin E inhibition. This means that at concentrations at and above  $\sim 0.1\%$  of vitamin E in tetradecane, reaction (3) is almost independent of vitamin E concentration. If we assume a completely homogeneous dispersion of vitamin E at 0.1 wt.% in tetradecane, the phenolic groups will be spaced at an average distance of  $\sim 12$  nm throughout the liquid, that is on average at  $\sim 6$  nm from any, randomly generated peroxy radical. At this average distance, it is not surprising that phenol groups can effectively migrate to and react with a large fraction of the peroxy radicals as they are formed and before they can self terminate or propagate. A similar general trend in vitamin E effectiveness on ketone group formation is apparent in HDPE (Fig. 6). From the initial rate of ketone formation at a given vitamin E concentration, it can be seen that vitamin E in HDPE is a less effective peroxy radical scavenger than in tetradecane. Because the antioxidant will be exclusively in the amorphous fraction ( $\sim 0.4$ ) of the HDPE, it is actually more than twice the average concentration in this oxidisable fraction. This relative lack of effectiveness probably results from constraints on additive mobility in the solid polymer. We have also shown that vitamin E is only weakly effective as an antioxidant during the post-irradiation phase of HDPE degradation, again possibly resulting from restricted mobility of the additive close to the long-lived radicals [16]. In a separate paper, we compare the relative effectiveness of vitamin E with other, conventional phenolic antioxidants [10].

## 5. Conclusions

Vitamin E is a very effective antioxidant both in a model, liquid alkane, (tetradecane) and in HDPE at close to room temperature.

FTIR can be used to follow changes in vitamin E in oxidising HDPE at close to room temperature. Formation of isolated hydroperoxide groups as a result of the vitamin E- peroxy radical reaction is clearly demonstrated.

Like other phenolic AO, vitamin E leads to quinones products after the abstraction of its phenolic H atom to deactivate peroxy radicals formed in  $\gamma$ -irradiation. Experiments in solution showed that different quinones are formed depending on the vitamin E concentration.

Because vitamin E can quite effectively retard the oxidation of HDPE during  $\gamma$ -irradiation, it should be

useful in polyethylene which is radiation sterilised as packaging materials or medical devices. However,  $\sim 0.075$  wt.% will be required for every 10 kGy dose.

Studies in model liquid alkanes can help elaborate broad changes in solid HDPE, but differences in radical and additive mobility limit their applicability.

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