

Studies on photodegradation of poly(vinyl chloride) accelerated by α -hydroperoxy-tetrahydrofuran

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A study of the role of THF, THF–O₂ charge-transfer complex and α -hydroperoxy-tetrahydrofuran (HOO–THF) in the photodecomposition of poly(vinyl chloride) (PVC) film cast from THF is presented. Detailed e.s.r. studies show that during u.v. irradiation (254 nm), THF and/or HOO–THF, oxy–THF free radicals are formed, which participate in the dehydrochlorination of PVC. The final products of photooxidation of THF are α -hydroxy-tetrahydrofuran (HO–THF) and butyrolactone, which give strong i.r. absorption bands at 1735 and 1789 cm⁻¹, respectively. The presence of THF residues in PVC films cast from this solvent should always be considered when thermal or photochemical studies are made.

INTRODUCTION

Tetrahydrofuran (THF) is a very good solvent for poly(vinyl chloride) (PVC). It is very difficult to remove the last 2–3% of solvent in a film cast from THF solution, even when the film is dried *in vacuo* or treated with methanol^{1,2}. A number of papers have reported studies of photodegradation and photo-oxidation of PVC cast from solution of THF^{1–9}. The THF may or may not play an important role in the photo-degradation of PVC. The mechanism of PVC photolysis is complicated and is still the subject of much speculation. Because most studies were made with PVC samples cast from THF solution, the role of this solvent in the photochemical processes should always be taken into consideration. The present study deals with the effect of THF and products of its photo-oxidation on the photo-oxidative degradation of PVC.

EXPERIMENTAL

Suspension-polymerized PVC (Pevikon S-602) was obtained from KemaNord AB (Sweden) in the form of a white powder. The manufacturers data are: Fikentscher *K* value 60, $\bar{M}_n = 46\,000$, $\bar{M}_w = 103\,000$, and polydispersity factor 2.2.

Tetrahydrofuran (THF) (analytical grade, Merck) was refluxed over sodium borohydride, distilled and stored under N₂.

α -Hydroperoxy-tetrahydrofuran (HOO–THF) was prepared by the oxidation of THF in the presence of 0.01 M 1-azoisobutyronitrile at 65°C¹⁰.

PVC films (~50 μ m) cast from THF solution (1 wt %) directly onto NaCl plates and THF placed in a 1 cm u.v. cell were irradiated with a Philips 125 low-pressure mercury lamp (relative energy at 254 nm = 100.00).

Infra-red studies were made on u.v.-irradiated PVC films

cast directly onto NaCl plates and on u.v.-irradiated THF solutions in a 0.01 cm NaCl cell using a Perkin–Elmer (Model 257) i.r.-spectrometer. The i.r. spectra were monitored every 30 min. The i.r. bands used to follow the concentration of butyrolactone and α -hydroxytetrahydrofuran (HO–THF) were 1789 and 1735 cm⁻¹, respectively.

The concentration of HOO–THF was determined by a modified iodometric titration¹¹.

Photo or thermal dehydrochlorination of PVC and PVC + HOO–THF samples was carried out in a simple quartz tube reactor, which could be heated electrically up to 220°C. The HCl evolved was trapped in a liquid trap filled with a 0.5 N AgNO₃ + 1 N NH₄NO₃ aqueous solution. The kinetics of dehydrochlorination were followed by gravimetric determination of precipitated AgNO₃.

Molecular weight distributions (*MWD*) were measured by gel permeation chromatography (Waters Associates Model ALC/GPC 201) with THF as solvent. All *MWD* curves were corrected for the broadening effect.

The electron spin resonance (e.s.r.) spectra were determined with a Bruker e.s.r. spectrometer using accessories for liquid and solid samples and low temperatures. The measurements included a study of free radicals formed at 77K from THF, HOO–THF, PVC, PVC + THF and PVC + HOO–THF at 77K using 254 nm irradiation.

The measurements of dynamic mechanical loss tangent were made for PVC and PVC + THF (~2 wt%) using a direct-reading viscoelastometer (Rheovibron Model DDV-II, Toyo Measuring Instrument Co., Japan) at 110 Hz and between –100° and 120°C.

RESULTS AND DISCUSSION

The retention of tetrahydrofuran (THF) in PVC films after casting from THF solution is well-established². The presence of THF causes a rapid density change due to evaporation of the THF residue during heating to 120°C.

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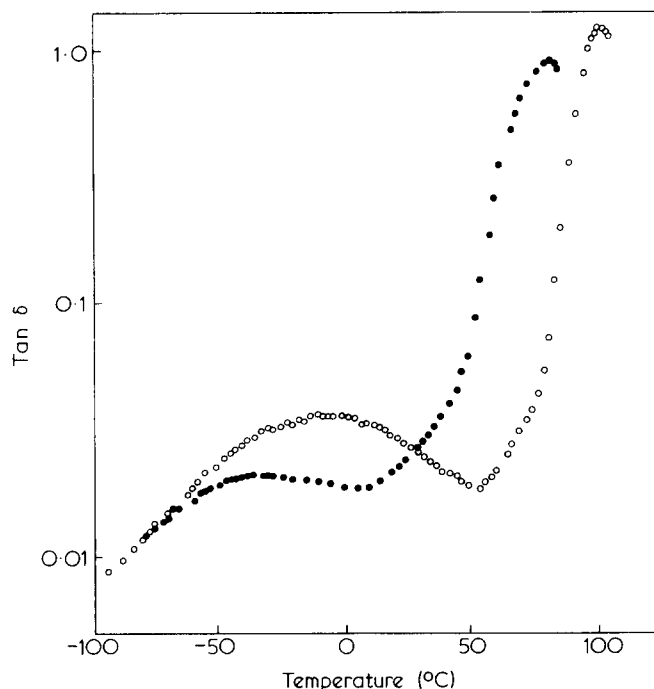


Figure 1 Tan δ versus temperature from dynamic mechanical measurements: \circ , for pure PVC and \bullet , for PVC-THF (2 wt%)

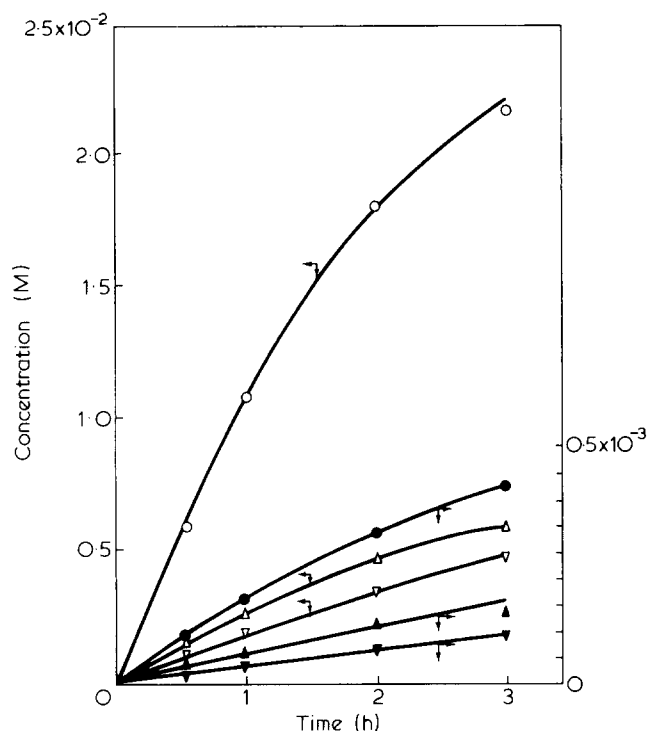


Figure 2 Kinetic curves of formation for: \circ, \bullet , HOO-THF; $\triangle, \blacktriangle$, HO-THF and $\nabla, \blacktriangledown$, butyrolactone for pure THF (open symbols) and PVC-THF (2 wt%) (filled symbols) during u.v. irradiation (254 nm)

In the present study we have found a simple method for detecting retained THF in PVC film by measurement of the dynamic mechanical loss tangent (Figure 1). In the presence of 2 wt% of THF in PVC film, the β peak is shifted from -5°C (pure PVC) to -30°C for PVC-THF and T_g is shifted from 102°C (pure PVC) to 82°C for PVC-THF.

The finding that traces of THF are so difficult to remove from the PVC film indicates that intermolecular interaction (e.g. charge-transfer complexation) between THF and polymer segments may occur. THF acts here as a plasticizer, inter-

preted as an increase of the free volume in the polymer matrix. This effect was also derived from permeability measurements². THF molecules present in the PVC membranes facilitate movement of the polymer molecules in the polymer matrix. The segmental mobility of the polymer chain increases due to replacements of polymer-polymer with polymer-THF molecular contacts. THF appears to form a permanent gel with the polymer chains in the amorphous phase of the polymer.

In a previous paper we postulated that the photodegradation of PVC in the presence of air is influenced by residues of THF². To obtain more accurate arguments, we measured rates of product accumulation for the photochemical oxidation of pure THF and PVC-THF film (2 wt%) (Figure 2). Iodometric titration was used to follow the formation of HOO-THF and i.r. spectrometry to measure the concentration of HO-THF (1735 cm^{-1}) and butyrolactone (1789 cm^{-1}). The results obtained show that all the products HOO-THF, HO-THF and butyrolactone are formed in THF and PVC-THF with similar rate constants even for short irradiation times.

HOO-THF is not photochemically stable and photolyses rapidly during irradiation with 254 nm light (Figure 3) giving products such as HO-THF and butyrolactone. The photodecomposition of HOO-THF (1 wt%) in PVC matrix occurs more rapidly than THF (1 wt%) under a nitrogen atmosphere. Free radicals formed from photolysis of PVC probably initiate decomposition of HOO-THF. The kinetics of the photolysis of HOO-THF in THF are first order with respect to the peroxide concentration whereas the kinetics of photolysis of HOO-THF in a PVC

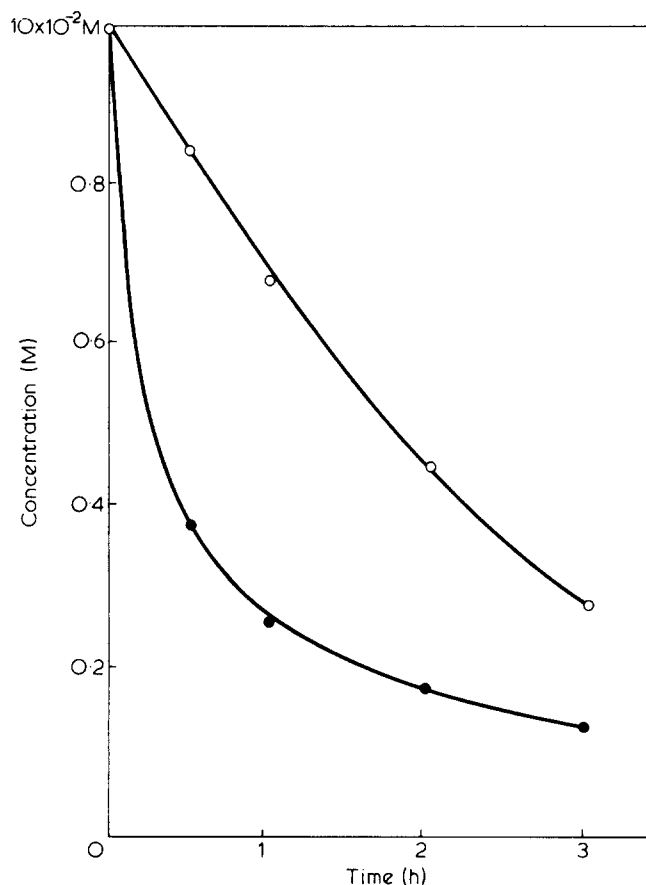


Figure 3 Kinetic curves of decomposition of HOO-THF: \circ , in THF (1 wt%); and \bullet , in PVC (1 wt%) during u.v. irradiation (254 nm)

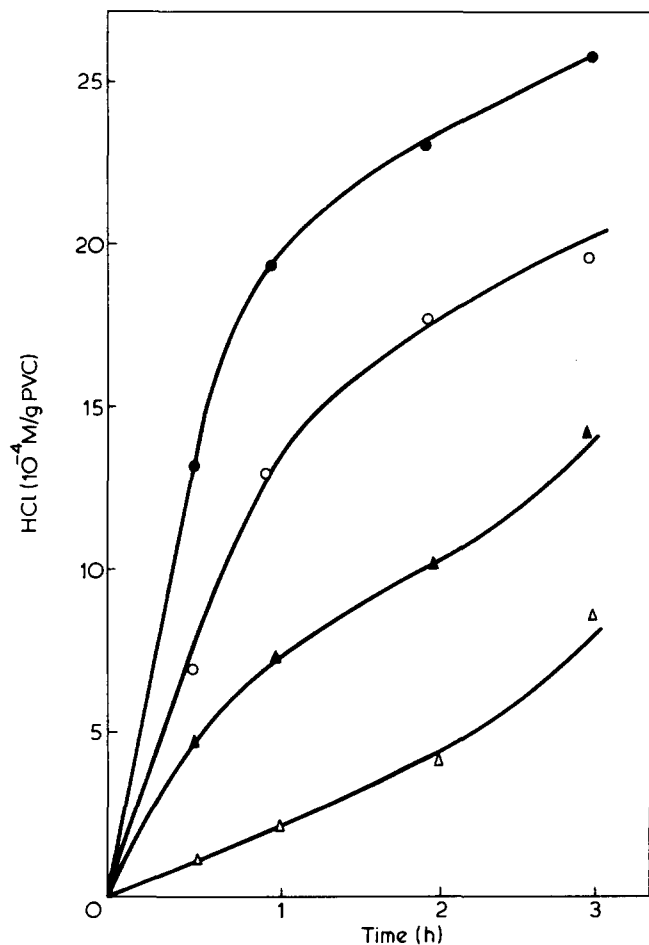
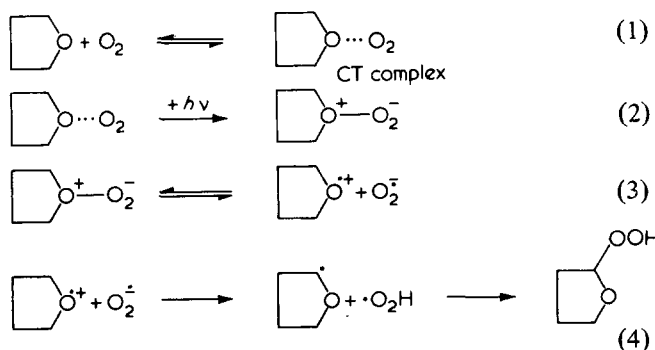


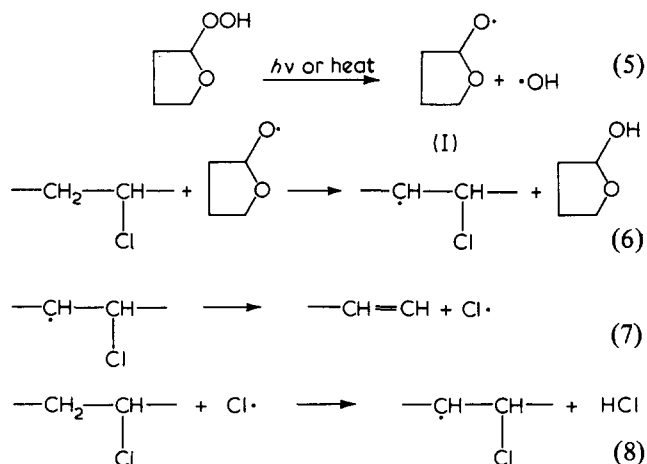
Figure 4 Kinetic curves of dehydrochlorination of PVC during: \circ, \bullet , thermal and $\triangle, \blacktriangle$, photodegradation. Open symbols for pure PVC and filled symbols for PVC+HOO-THF (1 wt %)

matrix are second order. Our results agree well with previously reported results on photo-oxidation of pure THF^{12,13}. Freshly-distilled THF in a contact with air immediately forms a THF-O₂ charge-transfer (CT) complex. This CT complex can not be decomposed by bubbling nitrogen through the solvent, for example. During u.v. irradiation, the CT complex is photolysed to HOO-THF, HO-THF and butyrolactone. If freshly-distilled THF is used to prepare PVC films in the presence of air it is impossible to avoid the presence of the THF-O₂ CT complex.

PVC film cast from THF probably contains residues in the form of both PVC-THF CT and PVC-THF-O₂ CT complexes. The formation of HOO-THF is a result of photolysis of a THF-O₂ CT complex, by the following mechanism:

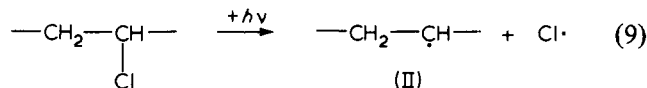


The HOO-THF (1 wt%) influence photo- and thermal (at 180°C) dechlorination of PVC (Figure 4). The amount of HCl evolved is much higher in the presence of HOO-THF. Free radicals formed from the thermal or photodecomposition of HOO-THF probably initiate free radical dehydrochlorination of PVC:



E.s.r. spectra obtained during u.v. irradiation (254 nm) of pure THF in the presence of air at 77K (Figure 5) show the formation of a single line spectrum, which can be attributed to the oxy-THF free radical (I). The same e.s.r. spectrum was obtained during the photodecomposition of pure HOO-THF under vacuum at 77K.

During u.v. irradiation (254 nm) of pure PVC at 77K a free alkyl radical (II) is formed which gives a six-line e.s.r. spectrum (Figure 6, broken line). This e.s.r. spectrum is symmetrical with a hyperfine splitting constant $\Delta H = 23$ G, a line intensity ratio of 1:4:9:9:4:1 and a *g* value of 2.0036. The e.s.r. investigation of the free radical (II) has been detailed previously¹⁴. The alkyl free radical (II) can be formed according to the reaction:



During u.v. irradiation (254 nm) of PVC-THF (~2 wt%) at 77K a free radical spectrum (II) from PVC is overlapped

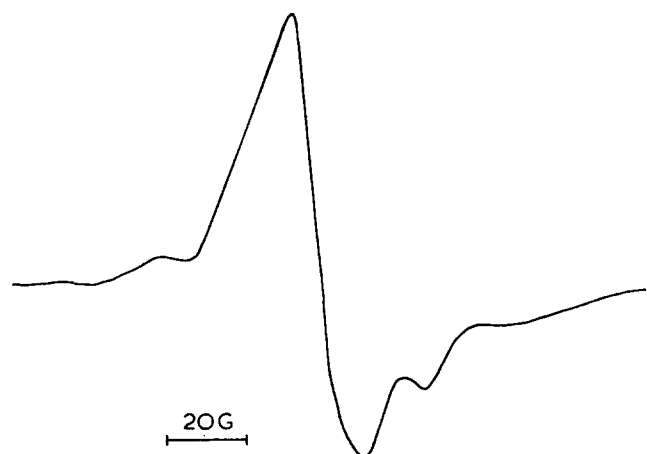


Figure 5 E.s.r. spectrum of free radicals formed during u.v. (254 nm) irradiation of pure THF (air saturated) at 77K. The same e.s.r. spectrum was obtained for photodecomposition of HOO-THF in vacuum at 77K

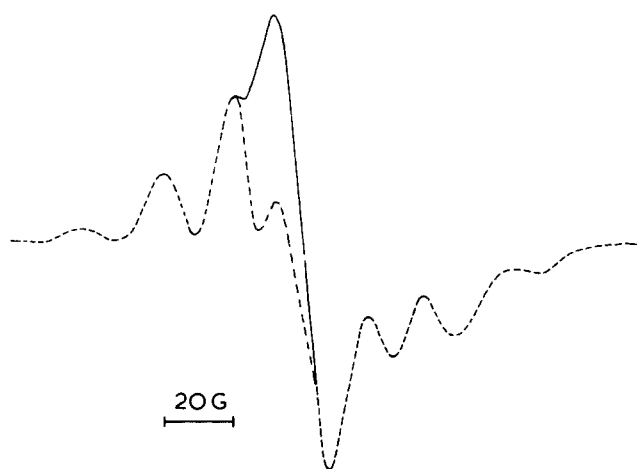


Figure 6 E.s.r. spectra of: (broken line) pure PVC u.v. irradiated (254 nm) at 77K; (solid line) PVC + THF (2 wt %) at 77K

by the spectrum of an oxy-THF free radical (I) (Figure 6, solid line). These results give evidence for the formation of two types of free radicals (I) and (II) during u.v. irradiation of PVC films casted from THF solution (PVC-THF).

The formation of oxy-THF radicals (I) in PVC film cast from THF during u.v. irradiation evidently influences the chain scission process. A characteristic shift in the molecular weight distribution curve can be observed for PVC + HOO-THF (1 wt%) when degraded by 254 nm irradiation in comparison with degradation of PVC irradiated under the same conditions (Figure 7). Formation of a high *MW* tail in the *MWD* curve also shows that oxy-THF radicals (I) participate in the crosslinking processes. The amount of insoluble gel was found to be ~23 wt% in PVC + HOO-THF (1 wt%) in comparison with ~11 wt% in PVC (pure).

Considering the data presented above and in previous papers^{2,15-17} it should be noted that THF residues have a considerable effect on the photodegradation of PVC. Step 1 is the formation of HOO-THF, which in step 2 easily photolyses to oxy-THF radicals. In step 3 the oxy-THF radicals may initiate dehydrochlorination of PVC, chain scission and crosslinking by free radical mechanisms.

CONCLUSIONS

The results presented give evidence of the role of THF solvent residues in the photodegradation of solvent-cast PVC. α -Hydroperoxy-tetrahydrofuran accelerates both photo and thermal dehydrochlorination of PVC by free radical mechanisms.

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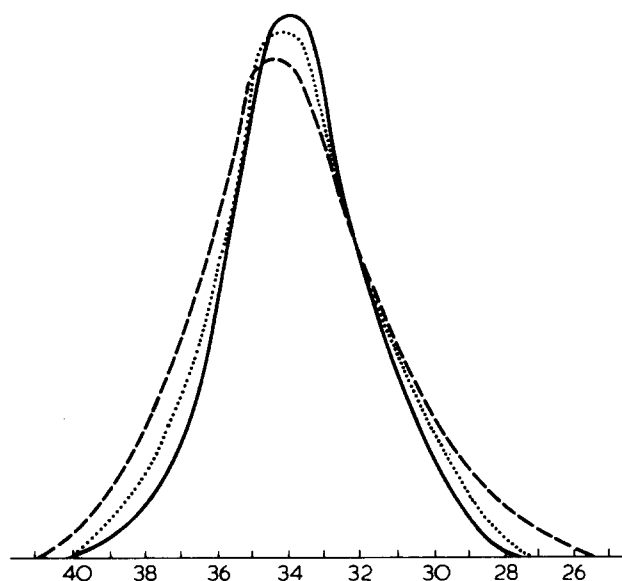


Figure 7 Normalized and corrected for broadening g.p.c. curves for: —, pure PVC; ····, pure PVC after u.v. irradiation (3 h, 254 nm), and - - -, PVC + THF (2 wt %) after u.v. irradiation (3 h, 254 nm)

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