

The Degradation of Poly(vinyl Chloride). II. Oxidative Degradation in Solution

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Synopsis

The results of studies on the oxidative degradation of poly(vinyl chloride) in a solvent, triphenyl phosphate, are described and compared with results previously reported for the oxidative degradation of bulk polymer samples. A range of chain-breaking and peroxide-decomposing antioxidants of the type commonly used to stabilize polyolefins were not effective in reducing the rate of dehydrochlorination of poly(vinyl chloride).

INTRODUCTION

The oxidative degradation of solid samples of poly(vinyl chloride) (PVC) has been well studied.¹⁻⁵ The rate of dehydrochlorination is considerably greater than under nonoxidative conditions and the reaction is autocatalytic. The oxidation of hydrocarbon polymers is free radical in nature,⁶ and often it has been assumed that the degradation of PVC in oxygen will involve free-radical intermediates.⁷ Peroxy radicals are thought to be involved, and antioxidants should be capable of slowing down or stopping the reaction. Rieche⁸ observed that the addition of hydroquinone suppressed the oxidative reaction slightly without affecting the nonoxidative degradation. Talamini⁸ reported that the addition of 0.06% of Topanol A, a substituted phenol, reduced the rate of dehydrochlorination almost to that obtained in the absence of oxygen. Also, Taylor⁹ has reported that resorcinol gave a slight measure of stabilization to PVC degraded under oxidative conditions. None of these authors observed a complete suppression of the oxidative reaction. This result is not unexpected since their experiments were carried out using solid samples, and a completely homogeneous mixture of components would not have been achieved.

Several authors^{10,11} have studied the oxidative degradation of plasticized PVC systems containing antioxidants, but they were more concerned with the stabilization of the plasticizers than of the PVC. Bengough¹² and, more recently, Braun¹³ have studied the oxidative degradation of PVC in a solvent, ethyl benzoate, but their results were not in agreement. Bengough observed no significant difference between degradation rate in

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oxygen and that in nitrogen, while Braun reported that degradation in oxygen was very much faster.

In this work, the oxidative degradation of PVC in solution was studied in more detail than previously reported, and the effect of antioxidants on the reaction was determined.

EXPERIMENTAL

The hydrogen chloride evolved during the thermal oxidative degradation of PVC was measured by continuous acid-base titration. Full details of the apparatus and technique are described elsewhere.¹⁴ For this work it was essential to use a solvent which was not susceptible to oxidation under the experimental conditions. Di(2-ethylhexyl) phthalate and ethyl benzoate were not suitable as they rapidly discolored and liberated acidic volatiles. Triphenyl phosphate was suitable and was used for all of the oxidation studies.

The PVC used was a suspension polymer with a number-average molecular weight of 51,000. Details of the preparation are given elsewhere.¹⁴

The antioxidants were used as supplied.

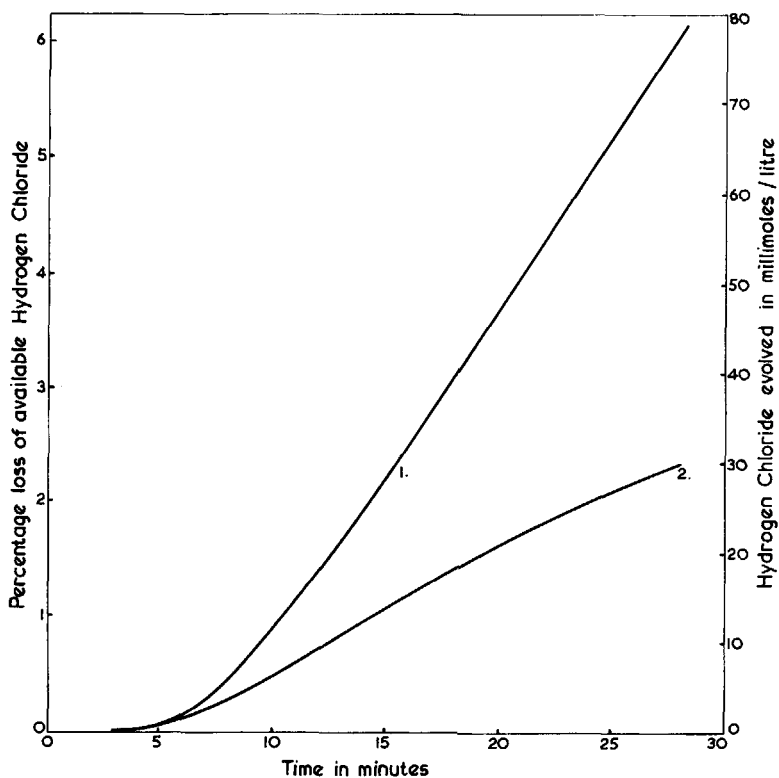


Fig. 1. Evolution of hydrogen chloride from PVC in triphenyl phosphate (80 g/l.) at 207.0°C with (1) oxygen, (2) nitrogen as carrier gas.

RESULTS

Degradation in Triphenyl Phosphate (TPP)

The rate of dehydrochlorination in oxygen at 207°C was constant (Fig. 1), in contrast to the decreasing rate observed using nitrogen as carrier gas.¹⁴ Oxygen flow rates between 20 and 180 ml/min had no significant effect.

Degradation rates were measured at different temperatures to enable calculation of the energy of activation E_a and the Arrhenius factor A for the reaction (Table I).

The effect of alternating nitrogen and oxygen as carrier gas in a degradation at 191°C is shown in Figure 2. Nitrogen was used until approximately 0.75% of the available hydrogen chloride had been lost from the polymer. On switching to oxygen, the dehydrochlorination increased rapidly to the "normal" oxidative rate. After 3.2% loss, a pure nitrogen supply was resumed, and the rate fell until finally (after about 5% loss) the nonoxidative rate was observed.

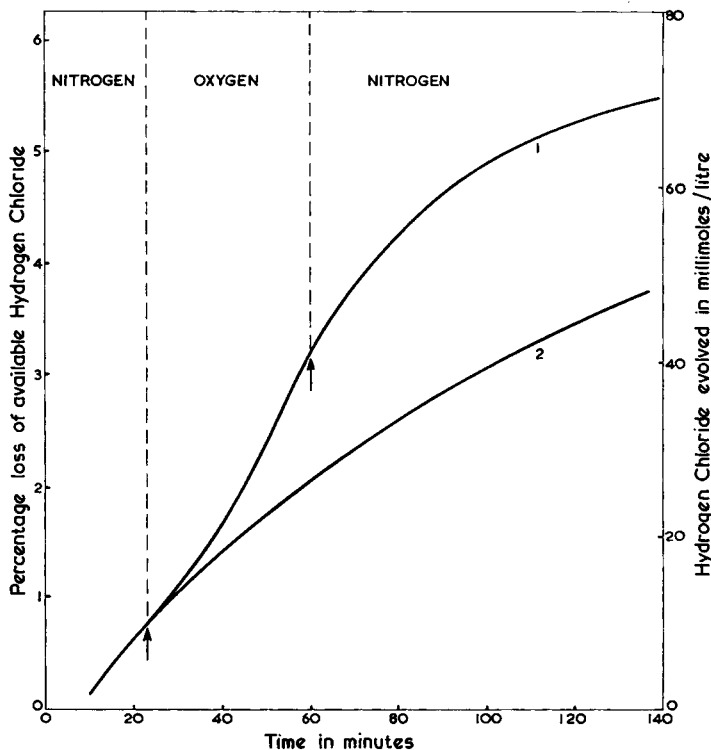


Fig. 2. Evolution of hydrogen chloride from PVC in triphenyl phosphate (80 g/l.) at 191.0°C with (1) nitrogen and oxygen alternately, (2) nitrogen alone as carrier gas.

TABLE I
Kinetic Parameters for Degradation in Oxygen of PVC in TPP

Temp., °C	Rate of degradation, ^a micromoles HCl/g PVC/min	E_a , kcal/mole	$A \times 10^9$, sec ⁻¹
170	2.72		
181	6.32		
191	13.55	31.3	8.5
207	42.2		

^a Measured at 1% loss of available hydrogen chloride.

Effect of Partial Pressure of Oxygen of Rate of Degradation

The results in Table II summarize the effect of the partial pressure of the oxygen (P_{O_2} , expressed as a fraction of the total pressure) on the rate of degradation in triphenyl phosphate.

TABLE II
Rates of Degradation at Various Partial Pressures of Oxygen^a

Partial pressure of oxygen P_{O_2}	$(P_{O_2})^{0.5}$	Rate, ^b micromoles HCl/g PVC/min
1.0	1.0	13.5
0.75	0.87	13.0
0.25	0.50	11.8
0.14	0.37	11.2
0.06	0.25	10.5
0.00	0.00	6.5

^a Temperature of degradation: 191.0°C.

^b Measured at 1% loss of available hydrogen chloride.

The rate of degradation is not directly proportional to the square root of the oxygen partial pressure (c.f., ref. 5), but there is a dependence of rate of degradation on oxygen pressure. The following equation describes the rate of oxidative degradation:

$$R_{O_2} - R_{N_2} = 7.0 \times 10^{-6} P_{O_2}^{0.2}$$

where R_{O_2} and R_{N_2} represent rates of dehydrochlorination in the presence and absence of oxygen, respectively.

Effect of Antioxidants on Rate of Degradation

The range of suitable antioxidants is limited since they must not be too volatile at the temperatures of the experiments and not give off acidic volatiles which will interfere with the estimation of hydrogen chloride. The antioxidants used were classified as shown below:

Phenolics. The effect of a range of phenolic antioxidants is shown in Table III. None of the phenolic antioxidants had any effect on the rate of the oxidative degradation of PVC at 170°C. Phenolic compounds act

as antioxidants by reacting with chain-propagating alkylperoxy radicals to form stable peroxidic structures. At high temperatures, however, these peroxides may themselves decompose to reinitiate the chain reaction. Phenolic antioxidants are therefore expected to be more effective at lower temperatures. Experiments carried out at 141°C, however, showed no significant reduction in rate in the presence of the antioxidant (Table III).

Quinones. The effect of a range of quinone-type antioxidants is shown in Table IV. The quinones did not reduce the rate of the oxidative degradation of PVC.

Amines. The effect of a number of amine antioxidants on the rate of oxidative degradation of PVC in TPP is shown in Figure 3. After an induction period, the length of which depended on the amine used, the reaction proceeded at a very much faster rate than in the absence of antioxidant.

TABLE III
Rates of Degradation Under Oxygen in TPP with Added Phenolic Antioxidants

Antioxidant	Antioxidant, wt-% (on PVC)	Rate, ^a micromoles HCl/g PVC/min	
		170°C	141°C
None	—	2.72	0.27
2,6-Di- <i>tert</i> -butyl-4-methyl-phenol	10	2.74	0.26
	50	2.81	—
	100	2.65	0.24
4,4'-Dihydroxydiphenyl	10	2.65	
	50	2.73	
	100	2.68	
2,2'-Dihydroxy-3,3'-di(α -methylcyclohexyl)-5,5'-dimethyldiphenylmethane	10	2.68	
	50	2.93	
	100	2.85	
1,3,5-Trimethyl-2,4,6-tris-(3,5-di- <i>tert</i> -butyl-4-hydroxybenzyl)benzene	10	2.96	0.28
	50	2.86	—
	100	2.92	0.27

^a Rates of degradation measured at 1% loss of available hydrogen chloride.

TABLE IV
Rates of Degradation Under Oxygen in TPP with Added Quinones

Antioxidant	Antioxidant, wt-% (on PVC)	Rate at 170°C, ^a
		micromoles HCl/g PVC/min
None	—	2.72
Hydroquinone	10	2.79
	100	2.81
Anthraquinol	10	2.76
	100	2.78
2,5-Di- <i>tert</i> -pentyl hydroquinone	10	2.83
	100	2.77

^a Rates of degradation measured at 1% loss of available hydrogen chloride.

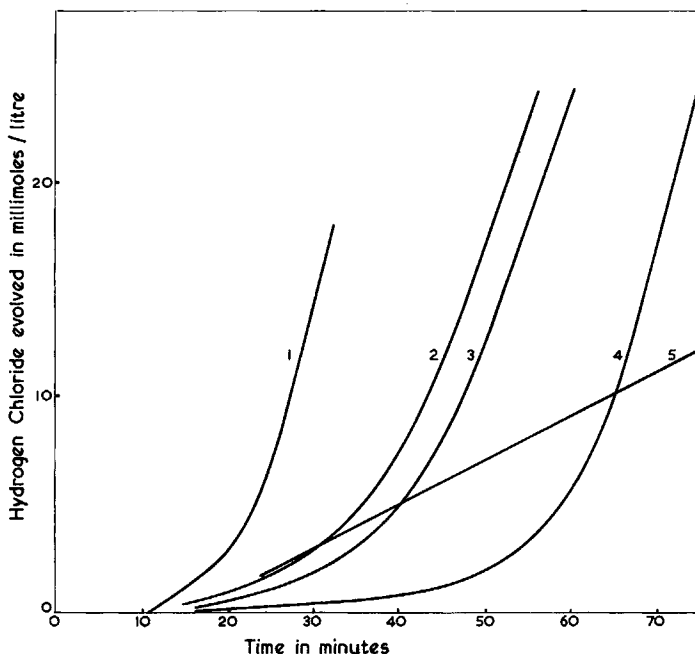


Fig. 3. Evolution of hydrogen chloride from PVC in triphenyl phosphate (80 g/l.) containing 5% (w/w on PVC) of various amine antioxidants at 169.5°C: (1) 4,4'-diaminodiphenylmethane; (2) phenyl- β -naphthylamine; (3) N,N'-diphenyl-*p*-phenylenediamine; (4) N,N'-di- β -naphthyl-*p*-phenylenediamine; (5) no antioxidant.

Other Antioxidants. The antioxidants described above are believed to function by interrupting the chain propagation reaction. The effects of two antioxidants, mercaptobenzimidazole and tri(nonylated phenyl) phosphite, which act through suppression of the initiation step of the oxidation, were also studied. These antioxidants, at a concentration of 5% by weight on PVC, had no effect on the rate of degradation at 170°C.

DISCUSSION

Like Braun,¹³ but unlike Bengough,¹² we have found that the rate of degradation of PVC was increased when oxygen replaced nitrogen as the carrier gas (Fig. 2). Since both of these authors used ethyl benzoate as the solvent, it is unlikely that the difference is caused by our use of triphenyl phosphate. We believe that the difference arises because Bengough¹² passed the carrier gas over the surface of the solution, whereas Braun and ourselves passed the gas through the solution. We have found triphenyl phosphate more suitable as a solvent since it does not degrade to produce volatile products.

We have found that the evolution of hydrogen chloride from PVC dissolved in triphenyl phosphate under oxidative conditions is constant and not autoaccelerating, in contrast to previous findings for solid samples.¹⁻⁵ Previously,¹⁴ we have attributed the difference in degradation behavior of

the solid polymer compared with a solution to the catalytic effect of the hydrogen chloride liberated. A similar effect might be expected under oxidative conditions. The constant rate of dehydrochlorination could be caused by continuous initiation by oxygen. Figure 2 shows that the higher rate of degradation was maintained only as long as oxygen was present. Very soon after reverting to nitrogen, the rate fell, indicating that labile sites introduced under oxygen did not have a very prolonged effect on dehydrochlorination. Similar conclusions were reached by Geddes² as a result of studies on bulk polymer samples.

The activation energy E_a for oxidative degradation (Table I) is very close to the value reported previously¹⁴ for degradation in triphenyl phosphate under nonoxidative conditions.

There is a dependence of rate of dehydrochlorination on oxygen pressure even at relatively high pressure (Table II), showing that a reaction involving oxygen is rate determining. This result contrasts with the behavior of many polyolefins on oxidation when the rate of reaction is independent of oxygen pressure at higher pressures.

The addition of large quantities of antioxidants such as phenols and hydroquinones had no effect on the rate of oxidative degradation of PVC in homogeneous solution. With polyolefins, these antioxidants react with alkylperoxy radicals to form comparatively unreactive hydroperoxides. It is possible, in the case of PVC, that such hydroperoxides were rapidly decomposed at 170°C, reforming active radicals. However, exactly the same effect was observed when experiments were made at 141°C (Table III). The results suggest that during the oxidative degradation of PVC in triphenyl phosphate, a steady-state concentration of chloroalkylperoxy radicals is never achieved.

Certain amines, sulfur-containing compounds, and phosphites inhibit the oxidation of polyolefins by suppression of the initiation step, i.e., by decomposing peroxides and hydroperoxides into nonradical products. Antioxidants of this type become increasingly efficient as the temperature is raised. These antioxidants did not reduce the rate of the oxidative degradation of PVC, and the amines actually caused a considerable increase in rate (Fig. 3). The latter result has been reported by a number of authors^{3,9,15} and is almost certainly due to a base-catalyzed elimination reaction.

In conclusion, the results suggest that the mechanism of loss of hydrogen chloride during the oxidative degradation of PVC in triphenyl phosphate may be quite different from the established mechanism for the autoxidation of polyolefins.

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