

The Photooxidation of Polymers.

III. Photooxidation of Polystyrene

N. GRASSIE and N. A. WEIR,*

Chemistry Department, The University, Glasgow, Scotland

Synopsis

In the photooxidation of polystyrene films at 28°C. under 2537 Å. radiation, water and carbon dioxide are the only significant volatile products. The intensity exponent of the reaction is unity under 600 mm. O₂ but zero under 20 mm., the quantum yield for oxygen absorption is 8.73×10^{-2} , the overall energy of activation is 6.0 kcal./mole, and the rate is independent of molecular weight. In addition, the rate is directly proportional to oxygen pressure, whether or not the total pressure is made up to 600 mm. with nitrogen. Investigation of the effect of film thickness shows that neither the nonuniform distribution of initiating radiation in the film nor the diffusion of oxygen influences the reaction rate abnormally. The free radical inhibitor 2,6-di-*tert*-butyl-4-methylphenol has no influence on the reaction, but the ultraviolet absorber 2-hydroxy-4-methoxybenzophenone accelerates oxygen absorption, having a maximum effect at approximately 3% concentration. It appears that the effect of ultraviolet absorbers is to protect the bulk of the polymer at the expense of the surface layer. Under 3650 Å. radiation the oxygen absorption is much slower and the reaction exhibits an induction period. From these results it appears that while the initially formed radicals react with oxygen to form ROO· and HOO· radicals, the next step in the Bolland hydroperoxidation mechanism, $RO_2 \cdot + RH \rightarrow ROOH + R \cdot$, is effectively suppressed by the lack of mobility of the long chain radicals within the solid polymer. The kinetic behavior described above can be accounted for qualitatively in terms of three competing processes, namely: (a) direct recombination of the primary radicals, R· and H·, (b) reaction of these primary radicals with oxygen, and (c) diffusion of the hydrogen atoms from the site of their formation.

I. EXPERIMENTAL

A. Measurement of Rate

The apparatus and methods described in the first paper of this series¹ were used. The lowest curve in Figure 1 illustrates the course of the oxidation reaction assuming the change in pressure in the apparatus is due to oxygen absorption. The rate measured by this curve has dropped to zero after only minute amounts of reaction have taken place.

A number of possible reasons for this apparent inhibition are immediately evident, including control of the rate of reaction by diffusion of oxygen, reduction of the effective light intensity by chromophores produced in the polymer in the early stages of reaction, and the production of radical reac-

* Present address: Meriot-Watt College, Edinburgh, Scotland.

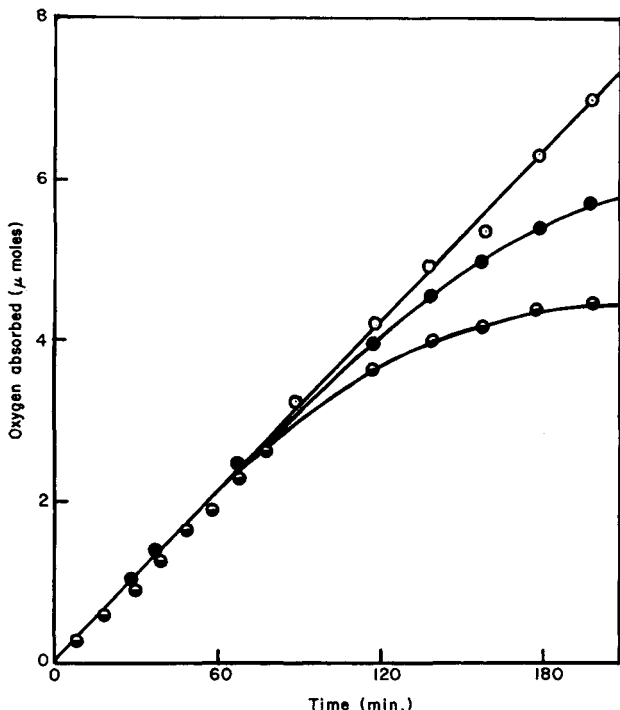


Fig. 1. Effect of carbon dioxide and water absorbers on the apparent course of the oxidation reaction: (●) no absorbers; (●) water absorber only; (○) water and carbon dioxide absorber.

tion inhibitors such as benzaldehyde.² None of these need be seriously considered, however, since as shown in Figure 1 small amounts of water and carbon dioxide absorbers (anhydrous magnesium perchlorate and Carbosorb, respectively) present in the system are sufficient to eliminate the curvature and give a constant rate over a long period.

While it is difficult to reconcile these results with any significant participation of the other factors mentioned above, they may become increasingly important in the later stages of the reaction. The data in Figure 1 imply that water and carbon dioxide are being formed in approximately equal amounts and that within 180 min. from the start of the reaction, they are together being produced as fast as oxygen is being absorbed. The induction period in their formation is probably a measure of the build-up of the primary product of oxidation in whose decomposition they are formed. Under these experimental conditions water and carbon dioxide appear to be the only significant products since gas-liquid chromatography and infrared analyses of the gaseous phase were always entirely negative.

B. Effect of Radiation Intensity

The intensity of 2537 Å. radiation incident upon the polymer was varied as described in the previous paper. Results at 600 mm. pressure of oxygen

are illustrated in Figure 2, and from the plot in Figure 3 an intensity exponent of unity (1.098) is obtained. At low oxygen pressures (20 mm.) the rate is seen in Figure 4 to be independent of oxygen pressure.

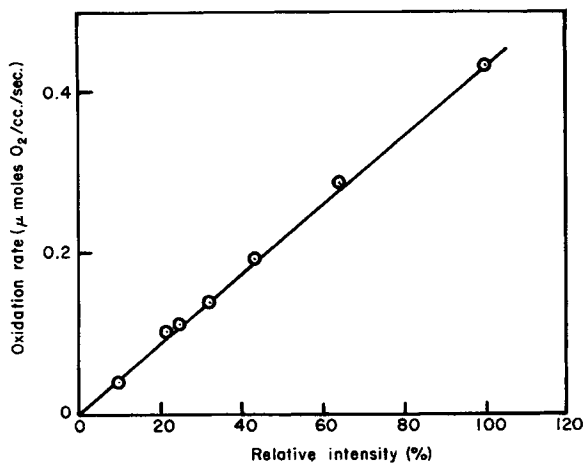


Fig. 2. Effect of light intensity on oxidation rate (oxygen pressure 600 mm.).

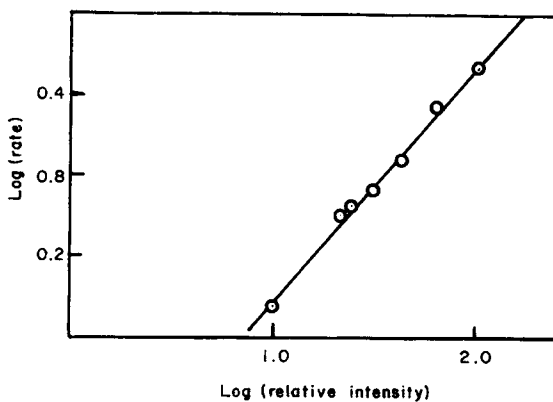


Fig. 3. Determination of intensity exponent for oxidation.

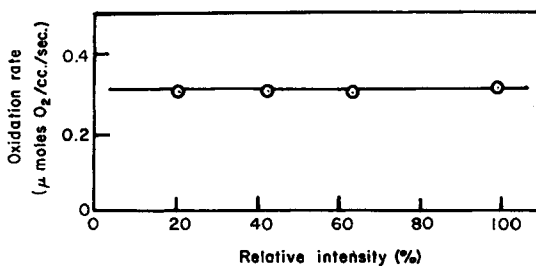


Fig. 4. Effect of light intensity on oxidation rate (oxygen pressure 20 mm.).

C. Quantum Yield

Since the rate of oxygen absorption by a 0.0044 mm. film under standard conditions is 1.93×10^{-10} moles/cm.²/sec. and the corresponding rate of absorption of 2537 Å. quanta is 2.21×10^{-9} einsteins/cm.²/sec. (see Part II³) the quantum yield is 8.73×10^{-2} .

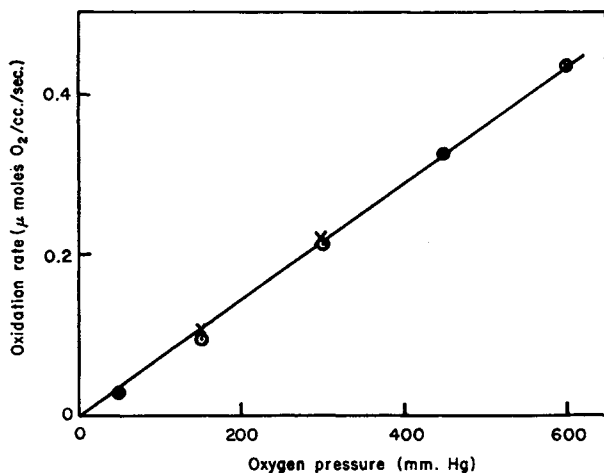


Fig. 5. Effect of oxygen pressure on oxidation rate: (O) pure oxygen; (X) added nitrogen to maintain total pressure of 600 mm.

D. Effect of Oxygen Pressure

Rates of oxygen uptake were measured under various oxygen pressures with the result shown in Figure 5, from which it is clear that the rate is directly proportional to the oxygen pressure.

This result is in complete disagreement with the observations of Bolland⁴ and Bateman,⁵ who concluded that in general for substances difficult to oxidize there was little if any pressure dependence above a few millimeters of oxygen. It was therefore suspected that in the present instance the

TABLE I
Rates of Oxidation of a Series of Polystyrenes
(Film Thickness = 0.0044 mm., Oxygen Pressure = 600 mm.)

Polymer	Rate of oxidation, μ moles O ₂ /cc./sec.	Initiator concentration, %	Molecular weight $\times 10^{-5}$
1	0.434	0.001	3.31
2	0.439	0.002	2.188
3	0.454	0.10	1.86
4	0.415	0.20	1.59
5	0.430	0.40	1.50
S1	0.434	0	4.93
SG3	0.443	0	15.1

effect might be an artifact of the system, possibly associated with the rate of diffusion of oxygen or of the products within the polymer. The above series of experiments were therefore repeated, the total pressure in the system being held constant at 600 mm. by addition of the appropriate amount of nitrogen. The results, also presented in Figure 5, are seen to be identical, within the limits of experimental error, with the previous series.

E. Effect of Molecular Weight and Initiator Fragments

Table I shows that the rates of oxidation of the series of polymers already mentioned in the previous paper² are independent of molecular weight and initiator.

F. Effect of Temperature

Rates of oxidation were obtained at a series of temperatures in the range 28–57°C. From the log rate versus $1/T$ plot in Figure 6 a value of 6.0 kcal./mole may be deduced for the overall energy of activation.

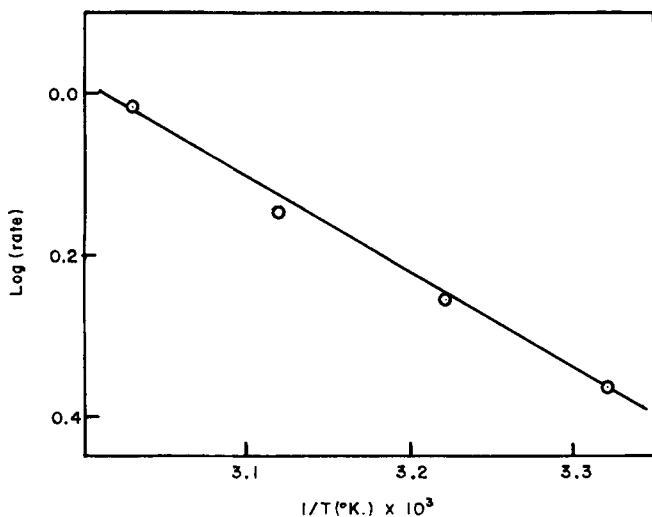


Fig. 6. Overall energy of activation of the oxidation reaction.

G. Effect of Film Thickness

In view of the nonuniform distribution of initiating radiation throughout the film and the possibility of the diffusion rate of oxygen having a bearing on the overall rate of the reaction, it is important to discover whether the unexpected rate versus oxygen pressure relationship described above can be accounted for in terms of these two factors. In order to eliminate the possibility of these two factors somehow playing a part, it is sufficient to show that in films of different thicknesses, under otherwise similar conditions, the overall rate of reaction is proportional to the amount of light absorbed.

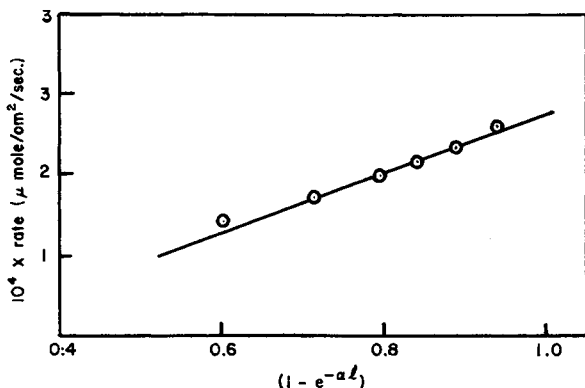


Fig. 7. Effect of amount of light absorbed on oxidation rate.

The proportion of the incident radiation absorbed by a film of given thickness may be calculated as follows. If I' is the number of quanta absorbed in unit area of a layer of thickness dl at a depth x from the surface (where all units are centimeters) on which radiation of quantum flux I_0 is incident, then

$$\begin{aligned} I' &= d[I_0(1 - e^{-\alpha x})]/dx \\ &= \alpha I_0 e^{-\alpha x} \end{aligned}$$

in which α is the extinction coefficient. Over the thickness l of the film the radiation absorbed is thus given by

$$\begin{aligned} \int_0^l \alpha I_0 e^{-\alpha x} dx \\ = I_0(1 - e^{-\alpha l}) \end{aligned}$$

If at every level throughout the thickness of the film the rate is proportional to the intensity then,

$$\text{Overall rate} = KI_0(1 - e^{-\alpha l})$$

The proportionality between rate and $(1 - e^{-\alpha l})$ is illustrated in Figure 7. Thus, like the radiation intensity, the oxidation rate is exponentially attenuated across the film. The value of α for polystyrene with 2537 Å. radiation is found to be 4210 (centimeter units). Thus it can be calculated that absorption of 2537 Å. radiation is almost complete across 0.01 mm. film. It follows, therefore, that photooxidation of styrene will take place only in a very thin surface layer, the bulk of the polymer being relatively unaffected.

H. Effect of Wavelength

The characteristics of oxygen absorption with the use of 3650 Å. radiation (the Osram lamp whose spectral characteristics are described in Part I¹)

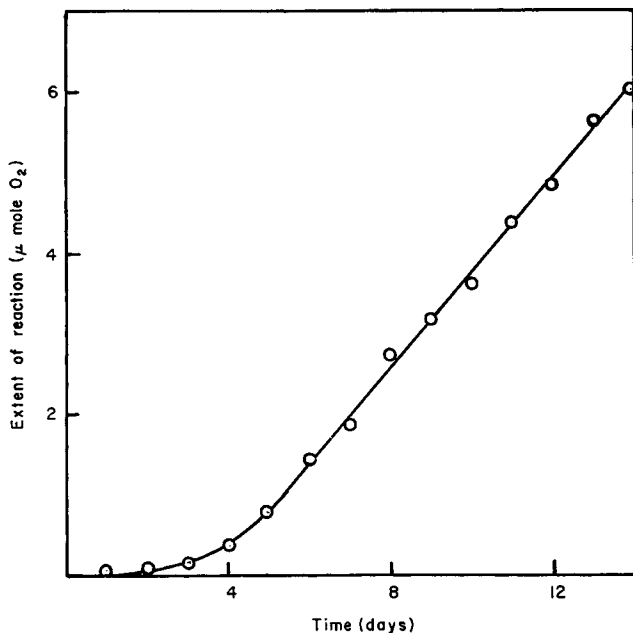


Fig. 8. Course of oxidation reaction under 3650 Å. radiation.

are illustrated in Figure 8. The characteristics of oxygen absorption are fundamentally different from those obtained with 2537 Å. radiation. An induction period of 90 hr. is followed by a constant rate of about $1/40$ that for the reaction initiated by approximately one-eighth the quantum intensity of 2537 Å. radiation.

I. Free Radical Inhibitors

Bolland⁶ showed a considerable time ago that small amounts of radical inhibitors like phenols and aromatic amines lead to induction periods in oxidation reactions. Although compounds of these types are used to stabilize polymer systems, information regarding their ability to suppress photooxidations is limited.

In order to assess ability purely to inhibit the reactions occurring it is clearly important that the material should not absorb strongly at 2537 Å., since it might either act as a photosensitizer or alternatively inhibit due to its effect in reducing the intensity. It is also clearly important in the preparation of films for test that the material should have a suitable common solvent with polystyrene and be compatible with solid polystyrene so that it may be uniformly incorporated in the films.

2,6-di-*tert*-butyl-4-methylphenol has both of these properties, and its ultraviolet spectrum is shown in Figure 9. This material is a very effective inhibitor of the polymerization of styrene. However, no induction periods or changes in rate were observed in the photooxidation of polystyrene, even in presence of concentrations as high as 1%.

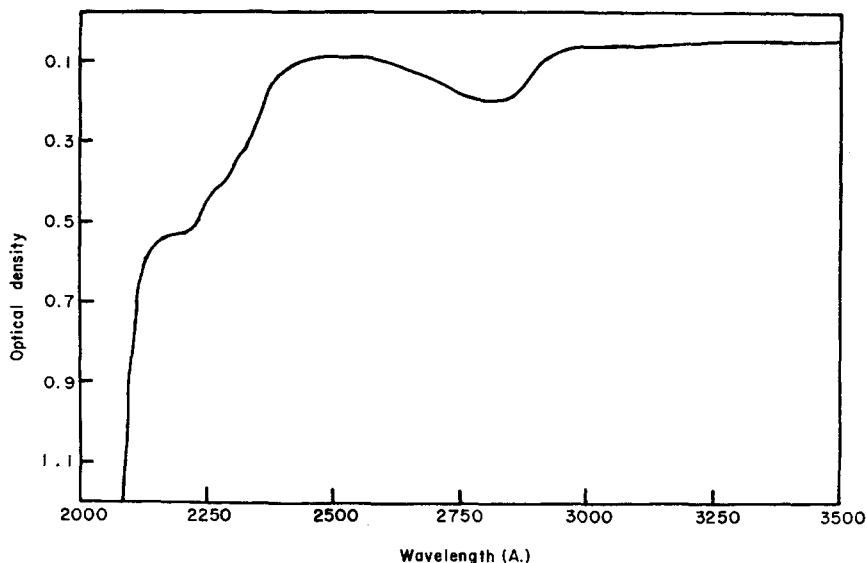


Fig. 9. Ultraviolet absorption spectrum of 2,6-di-*tert*-butyl-4-methylphenol.

J. Oxidation in Presence of Light Absorbers

Compounds related to 2-hydroxybenzophenone are effective inhibitors of photochemical reactions by virtue of their ability to absorb strongly the activating radiation. 2-Hydroxy-4-methoxybenzophenone was chosen for study because of its compatibility with polystyrene. Concentrations in the polystyrene film up to 6% were studied, and the effect on the rate of oxidation of the polystyrene is shown in Figure 10. Clearly the rate is accelerated throughout the range 0-6% but shows a maximum at approximately 3% absorber.

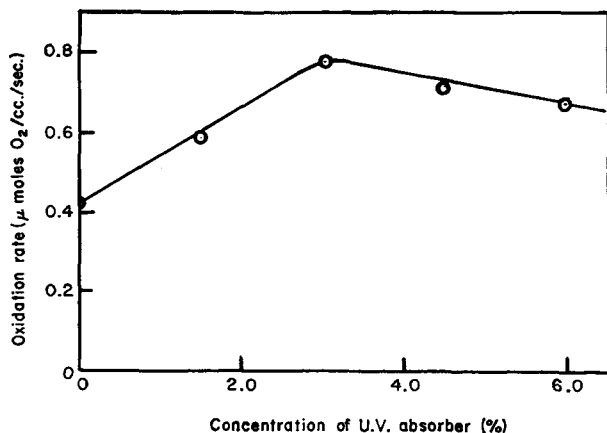


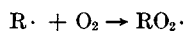
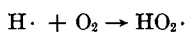
Fig. 10. Effect of 2-hydroxy-4-methoxybenzophenone on the oxidation reaction.

This acceleration is an indication that the ultraviolet absorber is either acting as a photosensitizer or is itself being oxidized, and this is supported by Hirt and Schmitts⁷ recent findings that high vacuum irradiation of ultraviolet absorbers of this type with 2537 Å. quanta results in appreciable photolysis. In all probability these photolysis products, being radical in nature, could either attack the polystyrene or themselves add oxygen.

The maximum rate at 3% absorber concentration may be explained qualitatively in terms of progressively more of the activating radiation being absorbed in the surface layers as the concentration of absorber is increased so that the amount of polystyrene capable of being oxidized decreased. It is perhaps significant to note that whereas concentrations of 2–5% of ultraviolet absorber are recommended commercially, concentrations of about 10% would be required to decrease the overall rate of oxidation to a value less than that of the pure polymer. The effect of the ultraviolet absorber thus appears to be to protect the bulk of the polymer from photooxidation, the surface layers being sacrificed in the process.

II. MECHANISM AND KINETICS OF PHOTOOXIDATION

It has already been shown in Part II³ that the high vacuum irradiation of polystyrene with 2537 Å. radiation results in fission of C–H bonds with the production of hydrogen atoms. Since this is purely a photochemical process it is unlikely that the presence of oxygen molecules, which do not absorb these quanta, will alter it fundamentally. Because of the radical properties of oxygen, this photoinitiation step will be followed by the rapid combination of the hydrocarbon radicals and hydrogen atoms so formed with oxygen to form the corresponding peroxy radicals,



For the reasons already discussed³ it seems that these hydrocarbon radicals will most likely be those formed by removal of the tertiary hydrogen atoms on the chain backbone.

According to the Bolland hydroperoxidation mechanism these peroxy radicals would abstract further hydrogen atoms from the polystyrene molecules to form hydroperoxide:

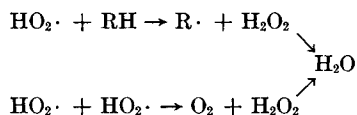


It has been shown that in the oxidation of small olefinic molecules, this, the vital step in the chain reaction, is strongly influenced by steric factors. For example, low kinetic chain lengths for oxidation are associated with systems in which hydrogen abstraction is sterically difficult. It is obvious that the corresponding step in polystyrene oxidation is going to be particularly difficult because of the bulk and lack of mobility of the radicals in the solid material, and indeed the low overall quantum yield, the inactivity of radical inhibitors and the intensity exponent value of unity all suggest that the subsequent chain process is effectively suppressed in this way.

In this connection it may be relevant that the quantum yield for oxidation, measured by oxygen uptake, is approximately twice that for photolysis, measured by the production of hydrogen. Thus for each act of initiation, which is assumed to be the same in both processes, one molecule of hydrogen is ultimately produced according to the mechanism proposed in Part II,³ while two molecules of oxygen are required to combine with the hydrocarbon radical and hydrogen atom produced.

It has been observed that crosslinking is concomitant with oxidation, and this, as in the photolysis reaction, can be accounted for in terms of combination of long-chain radicals. Crosslinking will of course decrease further the mobility of the chain radicals so that their destruction may be progressively inhibited, and indeed it has been demonstrated both by paramagnetic resonance⁸ and by chemical studies⁹ that oxidized polymer contains residual radicals.

It is much more difficult to explain convincingly the origin of the volatile products, H₂O and CO₂, why they are the only products, and why they are ultimately formed at a rate approximately equal to the rate of absorption of oxygen as shown in Figure 1. Water could be an ultimate product of the reaction of HO₂· radicals which may abstract hydrogen atoms from the polymer structure or react in pairs,



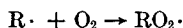
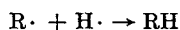
but carbon dioxide could only result from decomposition of the main polymer chains, in which case other volatile products should be expected to appear. It seems, therefore that the appearance of carbon dioxide and water as the only volatile products is an artifact of the system. Wall and his associates¹⁰ have shown that under ultraviolet radiation at 118°C. in oxygen a variety of products, including CO₂ and H₂O as the major constituents, can be detected by using mass spectrometry. In the present experiments at 28°C. it may be that only carbon dioxide and water are able to diffuse out of the rigid polymer film, the larger molecules produced in appreciable amounts being retained. In any case it is clear that the overall reaction is not limited to hydroperoxidation but that considerable subsequent decomposition occurs even at 28°C. in the solid polymer.

It has been demonstrated above that at all pressures the rate is proportional to the oxygen pressure. It is, however, proportional to and independent of light intensity at high and low pressures respectively, that is, at high pressures, rate = $KI(\text{O}_2)$; at low pressures, rate = $K'(\text{O}_2)$, where K and K' are constants and I is the radiation intensity. This is quite different from the kinetics of the hydroperoxidation radical chain process in which the rate is always proportional to the square root of the intensity and independent of or proportional to the oxygen pressure at high and low pressures,

respectively, which behavior is easily accountable on the basis of the Bolland mechanism.

A clue to the present behavior may be found in the photolysis reaction described in the previous paper in which the greater rate of development of unsaturation during photolysis carried out under greater nitrogen pressures was accounted for in terms of suppression of the diffusion from the site of their formation of the hydrogen atoms formed in the primary photolysis process. Thus the kinetic behavior of the oxidation reaction may be accounted for qualitatively in terms of three competing processes, namely, (a) recombination of the primary radicals $R\cdot$ and $H\cdot$, (b) reaction of the primary radicals with oxygen, and (c) diffusion of the hydrogen atoms from the site of their formation.

At high oxygen pressures, (c) is suppressed and there is direct competition between (a) and (b) which may be represented respectively by,



Thus since the concentration of radicals is proportional to the intensity, the overall rate which is given by the rate of reaction (b) must be proportional to both the intensity and the oxygen pressure.

At low oxygen pressures, on the other hand, (c) can occur more freely so that reaction (a) is effectively suppressed and the reaction rate depends only upon the availability of oxygen.

As shown in Figure 8, the characteristics of the reaction under 3650 A. radiation are different from those observed using 2537 A. radiation. The mechanism of the reaction must clearly be different since it was shown in the previous paper that under 3650 A. radiation photolysis of the polymer to produce hydrogen does not occur. It may be that photoactivated polymer molecules can react with oxygen in a different way to produce photolabile structures which can subsequently be photooxidized. This would account for the induction period.

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Résumé

Lors de la photooxydation de films de polystyrène à 28°C sous irradiation à 2537 Å, l'eau et l'anhydride carbonique sont les seuls produits volatils obtenus. L'exposant de l'intensité de la réaction est unitaire sous 600 mm d'O₂ mais zéro sous 20 mm, le rendement quantique vis-à-vis de l'absorption d'oxygène est 8.73×10^{-2} , l'énergie d'activation globale est de 6.0 Kcal/mole et la vitesse est indépendante du poids moléculaire. De plus, la vitesse est directement proportionnelle à la pression en oxygène, même si la pression totale est portée au dessus ou non de 600 mm au moyen d'azote. Des recherches sur les effets de l'épaisseur du film montrent que pas plus une distribution non-uniforme de la radiation d'initiation dans le film que la diffusion de l'oxygène n'influencent anormalement la vitesse de réaction. L'inhibiteur de radicaux libres, le 2,6-di-*tert* butyl-4-méthylphénol, n'a pas d'influence sur la réaction, mais l'absorbant des rayons UV, la 2-hydroxy-4-méthoxybenzophénone, accélère l'absorption d'oxygène, avec un maximum d'effet à une concentration de 3% approximativement. Il semble que l'effet des absorbants en U.V. est de protéger la masse du polymère aux dépens de la couche de surface. Sous une radiation de 3650 Å, l'absorption d'oxygène est beaucoup plus faible et la réaction montre une période d'induction. De ces résultats, il semble que tous les radicaux initialement formés réagissent avec l'oxygène pour former des radicaux ROO· et HOO·. Le mécanisme d'hydroperoxydation de Bolland suivant: $RO_2\cdot + RH \rightarrow ROOH + R\cdot$ est effectivement supprimé par le manque de mobilité des radicaux à longues chaînes dans le polymère solide. Le comportement cinétique décrit ci-dessus peut être exprimé qualitativement en trois processus compétitifs, à savoir: (a) recombinaison directe des radicaux primaires, R· et H·, (b) réaction de ces radicaux primaires avec l'oxygène, et (c) diffusion des atomes d'hydrogène depuis le siège de leur formation.

Zusammenfassung

Bei der Photooxydation von Polystyrolfilmen bei 28°C mit 2537-Å.-Bestrahlung sind Wasser und CO₂ die einzigen wesentlichen flüchtigen Produkte. Der Intensitätsexponent der Reaktion ist unter 600 mm O₂ eins, unter 20 mm jedoch null; die Quantenausbeute für die Sauerstoffabsorption beträgt $8,73 \times 10^{-2}$, die Bruttoaktivierungsenergie 6,0 kcal/Mol, und die Geschwindigkeit ist vom Molekulargewicht unabhängig. Zusätzlich ist die Geschwindigkeit dem Sauerstoffdruck direkt proportional, gleichgültig, ob der Gesamtdruck mit Stickstoff auf 600 mm gebracht wird oder nicht. Die Untersuchung des Einflusses der Filmdicke zeigt, dass weder die nicht einheitliche Verteilung der initiiierenden Strahlung im Film, noch die Diffusion des Sauerstoffs einen abnormalen Einfluss auf die Reaktionsgeschwindigkeit besitzen. Der Radikalinhibitor 2,6-Di-*tert*-butyl-4-methylphenol hat keinen Einfluss auf die Reaktion, der UV-Absorber 2-Hydroxy-4-methoxybenzophenon hingegen beschleunigt die Sauerstoffabsorption und besitzt bei einer Konzentration von näherungsweise 3% maximalen Einfluss. Es scheint, dass der Einfluss des UV-Absorbers in einem Schutz der Polymermasse auf Kosten der Oberflächenschicht besteht. Bei 3650-Å.-Bestrahlung ist die Sauerstoffabsorption sehr viel langsamer, und die Reaktion zeigt eine Induktionsperiode. Aus diesen Ergebnissen scheint zu folgen, dass immer die anfänglich gebildeten Radikale mit Sauerstoff unter Bildung von ROO— und HOO—Radikalen, den nächsten Produkten im Hydroperoxydationsmechanismus nach Bolland, reagieren, dass jedoch die Reaktion $RO_2\cdot + RH \rightarrow ROOH + R\cdot$ wirksam durch die mangelnde Beweglichkeit der Langkettenradikale im festen Polymeren unterdrückt wird. Das oben beschriebene kinetische Verhalten kann qualitativ durch drei kompetitive Prozesse wiedergegeben werden, nämlich: (a) direkte Rekombination der Primärradikale R· und H·, (b) Reaktion dieser Primärradikale mit Sauerstoff, und (c) Diffusion der Wasserstoffatome vom Ort ihrer Bildung.

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