

Oxidative Degradation of Polymers. VI. Photooxidation of Polystyrene Powder and Some Model Compounds

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The rates and products of photooxidation of polystyrene powder were studied at 70 °C under irradiation of a 30W low pressure mercury lamp. It was found that the rate of oxidation is remarkably high but the amount of oxygen incorporated into the polystyrene chain is very small. About a half of the absorbed oxygen appeared as carbon dioxide, independent of the conversion, irradiation time, oxygen pressure, and molecular weight. A trace amount of phenol was detected by GLC. The isotachophoretic analysis showed the formation of formic acid, oxalic acid, and glyoxylic acid. It was found that the mechanism of photooxidation is dependent on the state of the substrate, *i.e.*, crystalline solid, melt(viscous liquid) or solution. It is concluded that the polystyrene powder is photooxidized from its surface and aromatic ring of polystyrene is cleaved to give carboxylic acids. It was suggested that ozone played an important role in the photooxidation of polystyrene. The conclusions are supported by the results obtained in the photooxidation of some model compounds such as 1,2-diphenylethane, hexamethylbenzene, azobenzene, and phenylazotriphenylmethane.

Although it is accepted that the oxidation of polymers proceeds by a similar mechanism to that in the oxidation of simple hydrocarbons, the modes of polymer oxidation are complicated and need to be clarified.¹⁾ Photochemical oxidation of polymers has been studied by numerous investigators mostly on films.^{2,3)} Formation of hydrogen molecule was observed when polystyrene films were irradiated with 253.7 nm light *in vacuo*.^{4,5)} On the other hand, water and carbon dioxide were found as the only volatile products in the photooxidation of polystyrene films at 28 °C with 253.7 nm light.⁶⁾ Rabek and Rånby⁷⁾ proposed a new mechanism in the photooxidation of polystyrene as film or in benzene, where the cleavage of benzene ring plays an important role in the reaction pathway. They suggested the contribution of singlet oxygen molecule as a reactive species.

We have found that isotactic polypropylene powder is oxidized quite rapidly by irradiation with a 30 W low pressure mercury lamp, approximately half of the oxygen absorbed appearing as carbon dioxide independent of the extent of oxidation.⁸⁾ As an extension we have studied the photooxidation of polystyrene powder using a low pressure mercury lamp as a light source. The principal object is to measure rates and products of oxidation with particular attention on the absorbed oxygen balance. Polystyrene powder has an advantage over polypropylene powder in that it is soluble in organic solvents, making analyses of the oxidized polystyrene easier than for polypropylene. The data on the quantitative product analyses are lacking, but they are apparently most needed for the understanding of the nature of the reaction. Photooxidation of several relevant model compounds has also been carried out in order to elucidate the mechanism of the photooxidation of polystyrene.

Experimental

Materials. Polystyrene powders obtained from Presure Chemical Co. were used, the molecular weight being 4000, 9000, and 20400. 1,2-Diphenylethane (mp 52.5 °C) and azobenzene (mp 58 °C) were recrystallized twice from ethanol and benzene, respectively. Reagent grade hexa-

methylbenzene powder was used. The electronic spectrum of azobenzene in benzene solution shows two distinct maximum transition regions at 318 and 435 nm in the π - π^* and n - π^* , respectively. Thus the azobenzene is *trans*.⁹⁾ Phenylazotriphenylmethane was used without further purification. Commercial azobisisobutyronitrile (AIBN) and azobiscyclohexanecarbonitrile (ACN) were recrystallized from methanol and used as a radical initiator. Water was purified by passing through an ion-exchange resin.

A 30W low pressure mercury lamp was used as an ultraviolet light source, the main emission being the resonance lines of 184.9 and 253.7 nm.

Procedure. Fifty or one hundred mg polystyrene powder was weighed into a 50 ml quartz vessel. 10 ml of water was then introduced. The vessel was connected to a vacuum line and degassed by freeze and thaw cycles. Oxygen was then introduced. Amounts of initial and final gases were determined with use of a Toepler pump and by subsequent gas analysis by means of gas chromatography.⁸⁾

After the oxidation and analysis of the final gases non-condensable at -80 °C had been carried out, the vessel was opened and the reaction mixture was filtered with a glass filter 1G-4. The polystyrene powder recovered was washed several times with water, dried in a vacuum at 70 °C, weighed, and then analyzed by IR, NMR,¹⁰⁾ gel permeation chromatography¹¹⁾ and elemental analysis. The filtrate was analyzed by iodometric and neutralization titration. Low-boiling products were determined by gas liquid chromatography (GLC, Porapak-Q, 2 m, 50/80 mesh; PEG 20 M, 20 wt %, 7 m, 80/100 mesh). Low molecular weight acids were determined by isotachophoretic analysis with a Shimadzu Isotachophoretic analyzer IP-1B. Aqueous solution of 0.01 M glutamic acid was used as a terminal solution and aqueous solution containing 0.01 M L-histidine and 0.01 M L-histidine hydrochloride as a leading solution.

Results and Discussion

Photooxidation of Polystyrene Powder. The results of photooxidation of polystyrene powder of different molecular weight at different irradiation time are summarized in Table 1. Photooxidation was carried out under atmospheric pressure of oxygen. The rate of oxidation is remarkably great, the average rate of oxygen absorption being *ca.* 0.2 mol O₂/mol PS/h. The amount of oxygen absorbed per monomer unit of poly-

TABLE 1. PHOTOOXIDATION OF POLYSTYRENE POWDER AT 70 °C IN 10 ml WATER

Run No.	1	2	3	4	5	6	7	8	9
[PS] ₀ , μmol ^{a)}	495	471	490	490	978	954	960	960	961
Molecular weight	4000	4000	4000	4000	4000	4000	4000	9000	20400
Time, h	1/6	1.5	3	6	1.5	3	4.5	3	3
ΔO ₂ , μmol	18	190	385	718	322	509	1013	554	436
-dO ₂ /dt, mol O ₂ /mol PS/h ^{b)}	0.218	0.269	0.262	0.244	0.219	0.178	0.234	0.192	0.151
ΔO ₂ /[PS] ₀ , mol/mol ^{c)}	0.037	0.402	0.785	1.466	0.33	0.531	1.06	0.576	0.453
ΔCO ₂ , μmol	12	67	190	448	153	248	545	296	280
ΔCO ₂ /ΔO ₂	0.67	0.36	0.49	0.62	0.48	0.49	0.54	0.54	0.64
PS recovery, ^{d)} μmol		454	468	426	971		888	898	917
Calculated recovery, ^{e)} μmol		463	466	434	960		892	892	925

a) Initial polystyrene by monomer unit. b) Average rate of oxygen absorption by polystyrene monomer unit. c) The amount of oxygen absorbed per monomer unit. d) Polystyrene powder recovered after oxidation. e) See text for calculation.

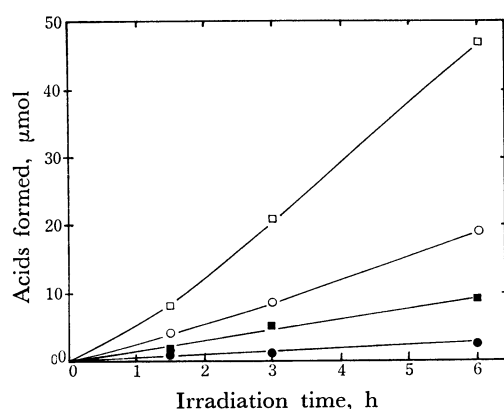


Fig. 1. Formation of carboxylic acids in the photooxidations of polystyrene powder (Runs 2, 3, and 4). □: Total acid, ○: formic acid, ■: glyoxylic acid, ●: oxalic acid.

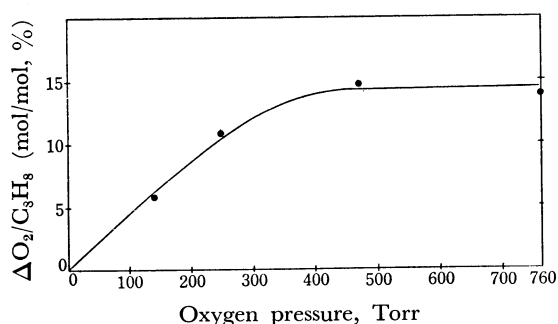


Fig. 2. Effect of oxygen pressure on the rate of photooxidation of polystyrene powder at 70 °C for 1 h.

styrene is as high as 0.80 mol/mol in 3 h and 1.50 mol/mol in 6 h (Runs 3 and 4). Nevertheless, approximately 90% of polystyrene powder could be recovered after photooxidation. This significance will be discussed later. About half of the absorbed oxygen was found as carbon dioxide. This is true even at 3.7% conversion, independent of irradiation time or the extent of oxidation. The effect of molecular weight of polystyrene is small both on rate and products of oxidation (Table 1).

It was found by isotachophoretic analyses that carboxylic acids such as formic, glyoxylic and oxalic acids

TABLE 2. ELEMENTAL ANALYSIS OF INITIAL AND PHOTOOXIDIZED POLYSTYRENES

Run No.	Initial PS		2	3	4
	Calcd	Obsd			
C, %	92.26	92.16	91.60	90.31	91.00
H, %	7.74	8.06	8.06	8.01	8.05
O, % ^{a)}	0		0.34	1.68	0.95
C/H	1/1.01	1/1.05	1/1.06	1/1.07	1/1.06
$\Delta\text{O}_2/\text{C}_8\text{H}_8$ obsd ^{b)}			0.001	0.056	0.031
$\Delta\text{O}_2/\text{C}_8\text{H}_8$ calcd ^{c)}			0.402	0.785	1.466

a) Oxygen content by difference. b) Calculated from the results of elemental analysis. c) Calculated from oxygen absorbed.

TABLE 3. RATIO OF AROMATIC HYDROGENS IN INITIAL AND PHOTOOXIDIZED POLYSTYRENES BY ¹H-NMR

			/	
Initial PS	Calcd	1	/	0.600
	Obsd	1	/	0.616
Run 5		1	/	0.621
7		1	/	0.610

are formed and their amounts increase with increasing irradiation time (Fig. 1). Hydroperoxide and hydrogen peroxide were also detected by iodometric titration in the presence and absence of catalase: for example, 6.8 μmol(2.1% based on absorbed oxygen) and 30.5 μmol(9.5%), respectively in Run 4. A trace amount of phenol was also found by GLC analysis.

The rate of oxidation increases with increasing oxygen pressure up to 400 Torr, further increase in oxygen pressure showing little effect (Fig. 2). Even at low oxygen pressures, carbon dioxide is the only gaseous product, about a half of the oxygen absorbed appearing as carbon dioxide.

Figure 3 shows the relation between conversion and the ratio of carbon dioxide formed to the oxygen absorbed. Although there is some scatter of data, the yield of carbon dioxide is approximately 50% of

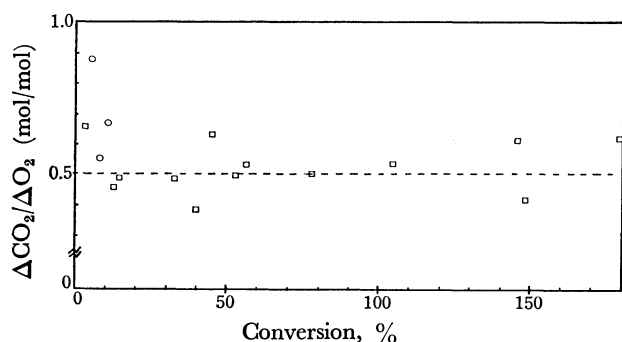


Fig. 3. Relation between $\Delta\text{CO}_2/\Delta\text{O}_2$ and conversion in the photooxidation of polystyrene powder. $\square$: $\text{Po}_2=1$ atm, $\circ$: Po_2 =reduced pressure.

the absorbed oxygen independent of conversion.

The results of elemental analyses of the initial and photooxidized polystyrene powders are summarized in Table 2. Although the amount of oxygen absorbed per monomer unit is quite high, the amount of oxygen incorporated into the polymer chain is exceedingly small, the ratio of carbon to hydrogen remaining constant. For example, 0.4 mol oxygen is absorbed per monomer unit, but little oxygen remained in the polystyrene (Run 2).

The ratio of aromatic to aliphatic proton for the initial and photooxidized polystyrenes obtained by integration of proton NMR spectra is given in Table 3. About 100 mg of polystyrene powder with molecular weight 4000 was used for analysis. The conversion based on monomer unit was 33 and 106% for 1.5 and 4.5 h irradiation, respectively. The ratio of aromatic to aliphatic proton remains constant.

Figure 4 shows the gel permeation chromatograms of initial and photooxidized polystyrene with molecular weight of 4000. Molecular weight distribution was shifted by oxidation to higher fractions rather than to

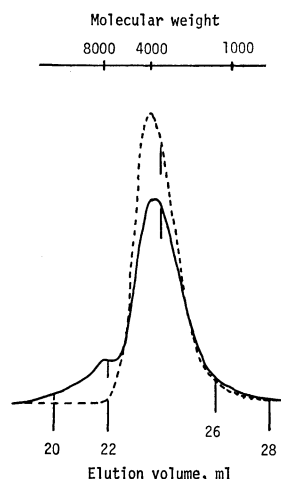


Fig. 4. Gel permeation chromatograms of photooxidized polystyrene powder. Molecular weight: 4000. ----: Initial polystyrene, —: photooxidized polystyrene.

lower fractions. Similar results were obtained for polystyrene with molecular weight of 9000 and 20400. The results indicate that crosslinking prevails over chain scission.

The results of photooxidation of polystyrene powder observed differ remarkably from those of thermal^{12,13} or even γ -ray¹⁴ oxidation of polystyrene at moderate temperature, where the major products are hydroperoxide, benzaldehyde and acetophenone with little carbon dioxide or carbon monoxide.

Oxidation of Model Compounds. In order to clarify the nature of the photooxidation of polystyrene powders, the photooxidation of several relevant model compounds was performed under similar conditions. 1,2-Diphenylethane and hexamethylbenzene were used as model compounds for aromatic hydrocarbons containing benzylic hydrogen (Table 4) while azobenzene

TABLE 4. OXIDATION OF 1,2-DIPHENYLETHANE(DPE) AND HEXAMETHYLBENZENE

Run No.	10	11	12	13	14	15	16	17 ^{c)}
DPE	Crystal ^{a)}	Crystal ^{a)}	Melt ^{b)}	Solution	Solution	Solution	Solution	Powder
μmol	505	502	520	1118	1050	1928	1935	635
Solvent	Water	Water	Water	Benzene	Benzene	Benzene	PhCl	Water
ml	10	10	10	5	5	3	3	10
Initiator						AIBN	ACN	
μmol						136	135	
Temp, °C	30	30	70	30	70	70	90	30
Time, h	1/6	2	2	2	2	4	4	2
Oxidation	Photo	Photo	Photo	Photo	Photo	Thermal	Thermal	Photo
ΔO_2 , μmol	73	481	661	251	257	162	244	257
$\Delta\text{O}_2/\text{DPE}$	0.14	0.96	1.27	0.22	0.24	0.08	0.13	0.40
ΔN_2 , μmol	0	0	0	0	0	83	83	0
ΔCO_2 , μmol	29	229	176	51	17	0	0	120
$\Delta\text{CO}_2/\Delta\text{O}_2$	0.40	0.48	0.27	0.20	0.07	0	0	0.48
ΔCO , μmol	0	0	60	90	107	0	0	0
Total acid, μmol		99	195	20	40	12	22	85 ^{d)}
Total peroxide, μmol		31	77	6	6	75	82	29

a) DPE crystal floating on the water surface. b) Viscous liquid of DPE floating on the water surface.
c) Hexamethylbenzene. d) 9.6 μmol formic acid and 50.8 μmol acetic acid were observed.

TABLE 5. PHOTO AND THERMAL OXIDATION OF AZOBENZENE AND PAT^c

Run No.	18	19	20	21	22
Substrate, RH	Azobenzene	Azobenzene	PAT	PAT	PAT
Substrate, μmol	515	515	297	502	1375
Solvent	Water ^{a)}	Water ^{b)}	Water ^{a)}	Benzene	Benzene
[RH], M				0.167	0.458
Oxidation	Photo	Photo	Photo	Thermal	Thermal
Temp, $^{\circ}\text{C}$	30	70	30	70	70
Time, h	2	2	2	2	3
ΔN_2 , μmol	30	42	44	527	1477
ΔO_2 , μmol	178	509	221	532	802
ΔCO_2 , μmol	96	234	72	0	0
ΔCO , μmol	0	4	0	5	Trace
$\Delta\text{CO}_2/\Delta\text{O}_2$	0.54	0.46	0.33	0	0
Recovered RH, μmol	483	433	284		
Total acid, μmol	29 ^{c)}	90 ^{d)}	56 ^{e)}		
Peroxide, μmol	16	81			
Carbonyl, μmol	Trace	Trace			

a) Substrate floating on the water surface. b) At 70°C , azobenzene is a viscous liquid and forms a thin layer on the water surface. c) Formic acid 14, glyoxylic acid 3, and oxalic acid $4\mu\text{mol}$. d) Formic acid 48, glyoxylic acid 12, oxalic acid 3, 2,4-hexadienedioic acid $6\mu\text{mol}$. e) Formic acid 34, glyoxylic acid 10, oxalic acid 4, 2,4-hexadienedioic acid $2\mu\text{mol}$.

and phenylazotriphenylmethane were used as model compounds that give phenyl radical (Table 5).

1,2-Diphenylethane is a crystal at 30°C , its photooxidation proceeding rapidly, and absorbs approximately equimolar oxygen in 2 h (Table 4, Run 11). The most striking result is that carbon dioxide is formed as a major product, its yield being as high as 40% of oxygen absorbed in spite of low reaction temperature and low conversion (Run 10). Essentially the same results were obtained at higher conversion (Run 11). After the photooxidation of 1,2-diphenylethane crystal, the reaction mixture was filtered and the recovered 1,2-diphenylethane washed and dried in a vacuum. The recovered diphenylethane was found to be identical with the initial, unoxidized 1,2-diphenylethane by GLC, NMR, IR, and elemental analyses. However, the formation of carbon dioxide decrease as 1,2-diphenylethane changes from crystal to melt and to solution, whereas the formation of carbon monoxide increase. The thermal oxidation initiated by AIBN or ACN gave neither carbon dioxide nor carbon monoxide and the major product was peroxide, the reaction being typical autoxidation. From the results of photooxidation of hexamethylbenzene powder (Table 4), oxidation is seen to be similar to that of polystyrene and 1,2-diphenylethane crystal. The rate is high, about half of the oxygen absorbed appearing as carbon dioxide. Carboxylic acids were another major product (33% based on oxygen uptake). Formation of acetic and formic acids suggests the cleavage of aromatic ring.

Azobenzene powder ($515\mu\text{mol}$) was floated on the water surface and irradiated with a low pressure mercury lamp at 30°C under atmospheric pressure of oxygen (Run 18). After 2 h, $178\mu\text{mol}$ oxygen was absorbed and $30\mu\text{mol}$ nitrogen and $96\mu\text{mol}$ carbon dioxide evolved. The isotachophoretic analysis of the aqueous phase showed the presence of $14\mu\text{mol}$ formic

acid, $3\mu\text{mol}$ glyoxylic acid, and $4\mu\text{mol}$ oxalic acid. These acids account for three quarters of the total acid observed by titration. After the oxidation was over, the powder floating on the water surface was collected, washed, and dried at room temperature in a vacuum. $483\mu\text{mol}$ Azobenzene was recovered, 99.6% of nitrogen being accounted for. The NMR, UV, IR, and elemental analyses for the recovered azobenzene gave identical results with those of the initial azobenzene. Thus, azobenzene should cleave photolytically to give nitrogen and phenyl radicals, which cleave to give eventually acids, carbon dioxide and other products.

The photooxidation of azobenzene was also carried out at 70°C (Run 19). Azobenzene becomes a viscous liquid when warmed to 70°C , forming a thin layer on the water surface. The nitrogen evolution did not increase appreciably with rise in temperature from 30 to 70°C . However, the amount of oxygen absorption at 70°C was about three times as much as that at 30°C . This can be ascribed partly to the phase change but mostly to the temperature difference. The temperature did not affect the product distribution, 46% of absorbed oxygen being found as carbon dioxide.

Phenylazotriphenylmethane (PAT) was oxidized either photochemically or thermally. Photooxidation was carried out with solid PAT, and thermal oxidation in benzene solution. The results show that considerable carbon dioxide was formed by photochemical oxidation, while in contrast, none was observed by thermal oxidation even at higher conversion (Table 5).

Mechanism and Active Species in the Photooxidation of Polystyrene Powder.

Polystyrene powder is oxidized remarkably fast by irradiation with a 30 W low pressure mercury lamp. Approximately half of the oxygen absorbed gives carbon dioxide even at low temperature and low conversion. The yield for carbon dioxide remains constant independent of the extent of oxidation.

TABLE 6. PHOTOOXIDATION OF POLYSTYRENE WITH AND WITHOUT H₂O FILTER^{a)}

Run No.	23	24
PS, ^{b)} μmol	960	978
H ₂ O, ml	10	10
H ₂ O filter	Yes	No
Temp, °C	24	24
Time, h	9	9
ΔO ₂ , μmol	298	882
ΔO ₂ /PS, %	31	90
ΔCO ₂ , μmol	81	404
ΔCO ₂ /ΔO ₂ , %	27	46
ΔCO, μmol	37	0
Recovery, μmol	923	910
Peroxide, μmol	5	149
Total acid, ^{c)} μmol	80	130
Formic acid, μmol	40	45
Glyoxylic acid, μmol	15	16
Oxalic acid, μmol	3	21
Malealdehyde, μmol	7	6
Maleic acid and/or 2,4-hexadienedioic acid, μmol	3	4
	68 μmol (85%)	92 μmol (71%)

a) 2.3 cm H₂O filter was placed between light source and quartz cell (3 cm). b) By monomer unit, molecular weight=4000. c) By titration.

That the photooxidation of polystyrene powder takes place exclusively on its surface is supported by the following results: (1) the oxygen incorporated into polymer chain is quite small in spite of high oxygen uptake (Table 2), and (2) much of the powders of polystyrene, azobenzene, PAT and 1,2-diphenylethane is recovered after photooxidation.

If we assume that one styrene monomer unit yields eight molecules of carbon dioxide and four molecules of water, then the remaining polystyrene is estimated by

$$\text{Calculated recovery (\%)} = 100 \times \frac{[\text{PS}]_0 - \Delta\text{CO}_2/8}{[\text{PS}]_0},$$

where [PS]₀ is the initial amount of polystyrene and ΔCO₂ is carbon dioxide formed. As shown in Table 1, the calculated recovery agrees well with the observed recovery. On the other hand, if we assume that aromatic carbons are not oxidized to carbon dioxide and only two molecules of carbon dioxide are formed from one monomer unit, the agreement between calculated and observed recoveries is poor.

Formation of low molecular weight carboxylic acids and the importance of crosslinking observed in this study indicate the contribution of ozone, since they resemble the ozonation of polystyrene¹⁰⁾ and aromatic compounds.¹⁵⁾ 184.9 nm light converts oxygen molecule into ozone,¹⁶⁾ which is decomposed to O(¹D) and singlet oxygen molecule by 253.7 nm light.¹⁷⁾ Since 184.9 nm light is absorbed by air, it was first assumed that only monochromatic 253.7 nm light would be introduced into the vessel.

In order to study the effect of wavelength of the incident light and contribution of ozone, photooxidation

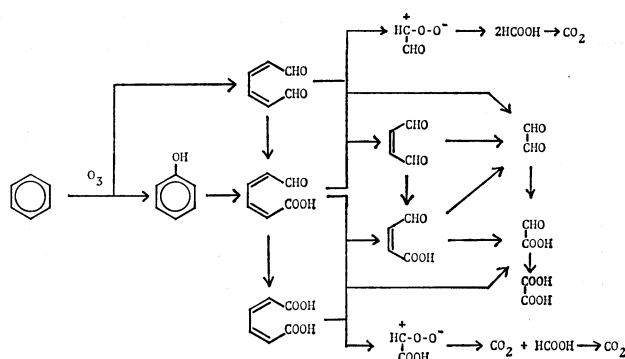


Fig. 5. Ozonation of aromatic ring. Substituents are neglected.

was carried out in the presence and absence of a water filter placed between light source and quartz vessel. The main emission of the light source is the resonance lines of 184.9 and 253.7 nm. The former should be absorbed by water. The results of photooxidation of polystyrene powder with and without a water filter are given in Table 6. We see that the water filter decreases both rate of oxidation and formation of carbon dioxide.

It should be noted that photooxidation of polystyrene gives formic acid, glyoxylic acid, oxalic acid, malealdehyde, and maleic acid and/or 2,4-hexadienedioic acid. The products are similar to the ozonation products from aromatic compounds,^{10,15)} strongly indicating the contribution of ozone in the cleavage of aromatic ring.¹⁸⁾ These products should be formed according to the scheme shown in Fig. 5. The formation of ozone in the reaction vessel was confirmed by passing the gas through an aqueous solution of potassium iodide.

However, it is not clear how carbon dioxide is formed in as high as 50% yield and why the yield decreases when the state of substrate changes from solid to melt and to solution.

Conclusion

Polystyrene powder was found to be oxidized rapidly when irradiated with a low pressure mercury lamp. The major product was carbon dioxide with approximately 50% yield based on oxygen absorbed. The yield is independent of irradiation time, oxygen pressure and molecular weight. The molecular weight did not decrease appreciably by oxidation, crosslinking being observed instead. Formic acid and other low molecular weight carboxylic acids were also observed. It was suggested that ozone plays an important role as an active species, especially in the cleavage of aromatic ring.

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