



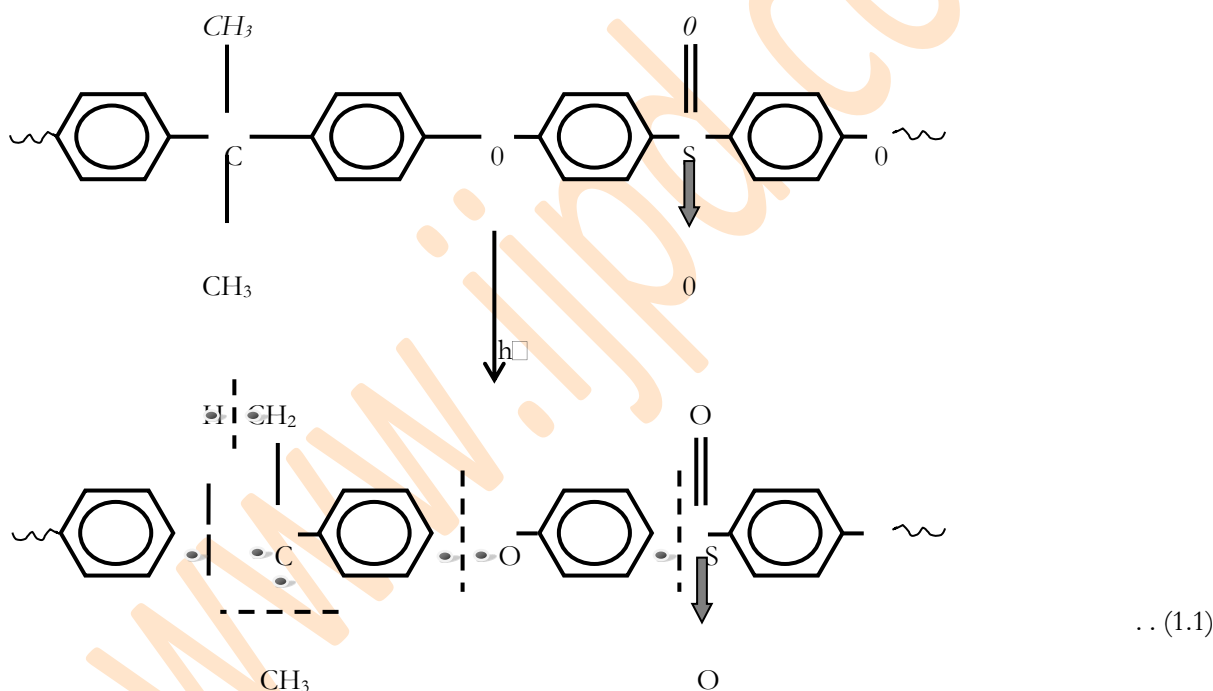
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One can see that unstabilized APS in the nonattendance and presence of Cust2 corrupt quickly under UV illumination since it assimilates light in the locale of 253.7nm. it isn't is really to be expected, that the openness of APS to UV light causes synthetic changes as confirmed by expansive ingestions in both the hydroxyl and carbonyl locales of the infrared range, characteristic of an assortment of oxidation

items. A concurrent diminishing in the methyl retention band at 1385 cm⁻¹ indicates that the methyl bunches are appended during photograph oxidation.

The results of photolysis Table (A.1) show the arbitrary scission of the polymer. In the commencement cycle, scission evidently happens at each bond aside from the fragrant C - C and C - H bonds Eqn. (1.1).



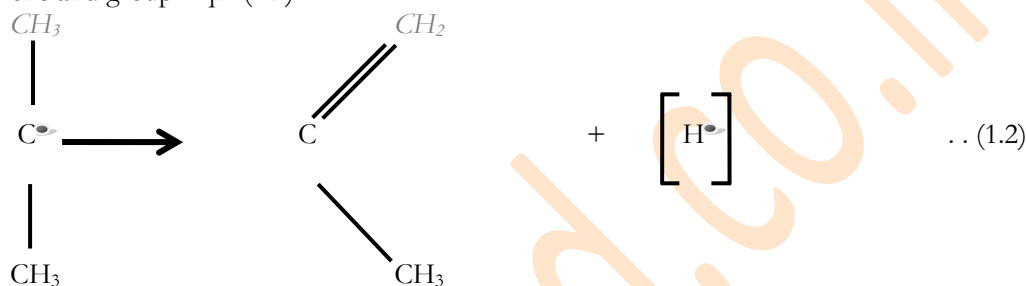
If isopropylidene radicals formed in this polymer decomposed by normal pathways, scission at the aromatic isopropylidene single

TABLE A.1: Gases found after U.V. Irradiation of APS films :-

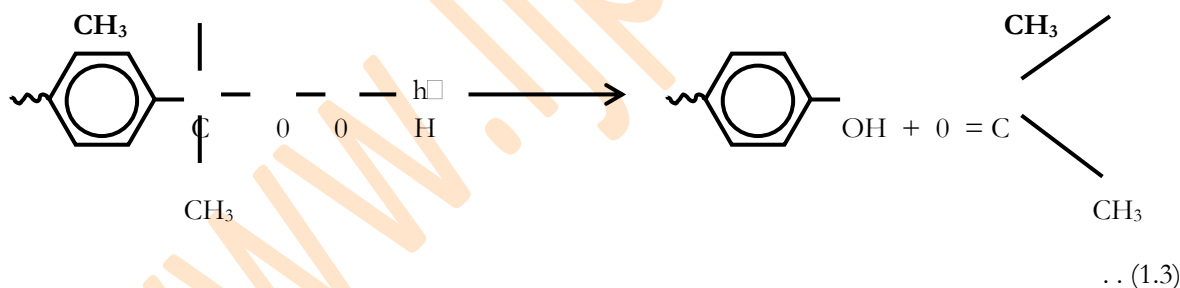
Constituents	Composition, Volume %	
	Photolysed in vaccum	Photolysed in oxygen-enriched air
Hydrogen	24.9	0.04
Water	Not detected	Not detected
Methane	1.8	0.13

Ethane	Trace	Not detected
Benzene	0.1	Trace
Carbon monoxide	40.9	9.5
Carbon dioxide	24.9	31.2
Nitrogen	2.0	56.4
Oxygen	2.3	0.02
Carbonyl sulfide	2.6	0.01
Sulfur dioxide	0.5	0.001
Carbon disulfide	Not detected	Trace
PV, mm-cc	40	10,000

Bond would appear to be quite infrequent. The isopropylidene radical should undergo both disproportionation and oxidation reactions. One product of the disproportionation reaction would contain a methylene and group Eqn. (1.2)



Oxidation would lead to cumene hydroperoxide and groups, which typically undergo decomposition to acetone and phenols, as shown in Eqn. (1.3).



Acetone was not detected in the evolved gases, and methylene bonds were not observed in the infra-red spectrum of aged polymer. We cannot discount, however, the possibility that both of these materials may have reacted with the oxysulfur acids and esters formed by other processes Eqn. (1.4 – 1.7).

Hydrogen most likely arises after C–H bond scission by quenching through aliphatic groups Eqn. (1.4).



.. (1.4) Methane can be formed after C–CH₃ bond scission by hydrogen abstraction Eqn. (1.5)



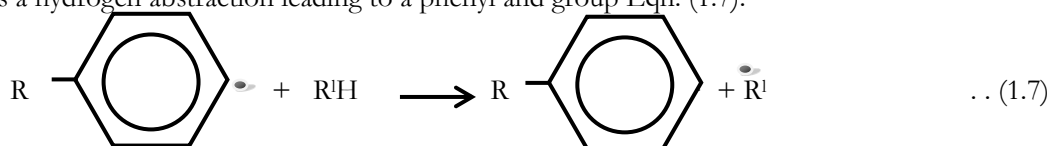
.. (1.5)

Traces of ethane can be explained by methyl abstraction, as shown in Eqn. (1.6).

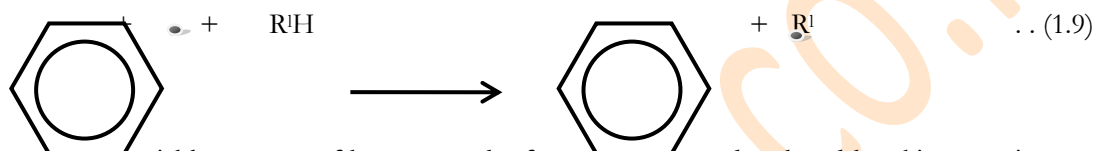
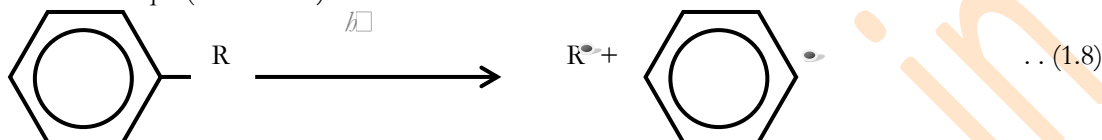


.. (1.6)

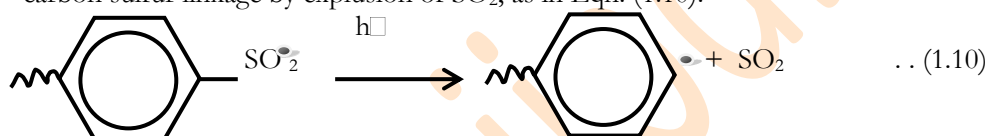
The formation of benzene required bond scission at both sides of an aromatic ring. The process probably involves a hydrogen abstraction leading to a phenyl and group Eqn. (1.7).



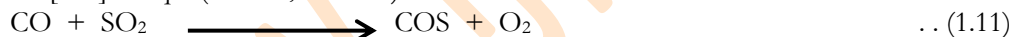
Photolytic scission at the terminal phenyl polymer C-C bond and quenching of the radical would give rise to benzene Eqn. (1.8 and 1.9).



For any appreciable amount of benzene to be formed the secondary bond breaking reaction must be at least as favourable as the initial scission processes. Sulfur dioxide undoubtedly arises after scission at the carbon sulfur linkage by explosion of SO₂, as in Eqn. (1.10).



Carbonyl sulfide and carbon disulfide can be formed by the interaction of carbon monoxide and sulfur dioxide [46] Eqn. (3.10.11, 3.10.12).



Little amounts of oxygen can be clarified by the responses of CO with SO₂. In the vacuum photolysis, how much oxygen important to account sensibly for the oxides of carbon should develop from polymer. The explosion of subatomic oxygen from polymer under these photolytic conditions would need to continue by preposterous components. The realities that sulfate isn't identified on the outer layer of the vacuum photolyzed polymer and that SO₂, a famous hydroperoxide forager is available in the advanced gases in more noteworthy sum than on account of photograph oxidation showed that the forerunners to the oxides of carbon aldehydes and carboxylic acids were at first present in the polymer and didn't emerge in view of oxidation during photolysis Eqn. (1.13).

No gauge of the degree of C-O or isopropylidene C-C bond breaking can be made, yet from the

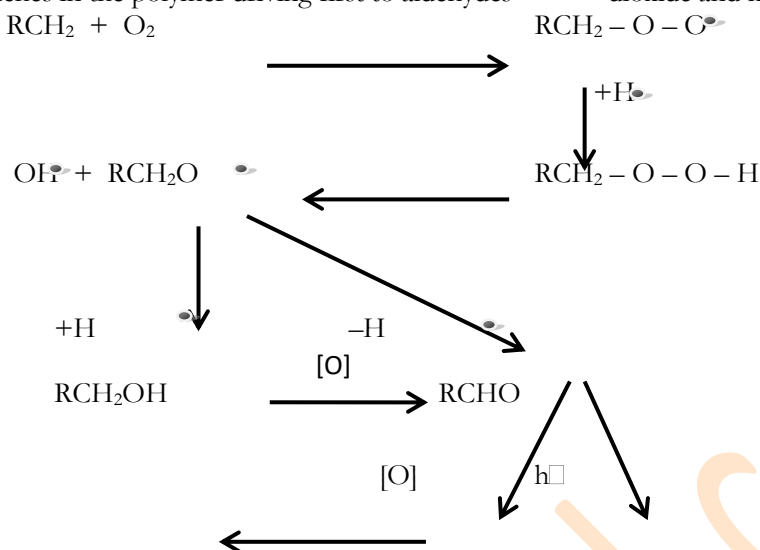
gases separated the request for other security breakage can be approximated. C-H bond cleavage measurably remedied is of a similar significant degree as C - S and C - CH₃ bond scission. It appears to be sensible to expect to be that C - O and isopropylidene C - C bond breaking would likewise be of this request greatness. As would be normal, optional breakage prompting benzene is the least in the request for scission.

The significant contrast between vacuum photolysis and photograph oxidation is the mind-boggling oxygen extinguishing response. During photograph oxidation the oxygen at first present is totally consumed. The chief gases framed are carbon monoxide and dioxide.

Likewise with benzene, optional responses should be answerable for the oxides of carbon. Within the sight of overabundance oxygen, these auxiliary responses are prevalent. The presence of

carbon monoxide and dioxide is expected, then, at that point, to the oxidation of the methyl bunches in the polymer driving first to aldehydes

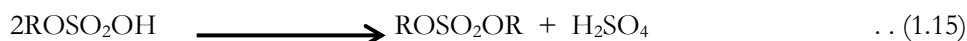
and carboxylic acids and afterward by decarboxylation and decarboxylation to carbon dioxide and monoxide Eqn. (1.13).



RH + CO₂ RCOOH RH + CO .. (1.13)

With the exception of methane, there is surprisingly little difference between the absolute amount of the remaining gases from photo-oxidation and from vacuum and photolysis. Carbon disulfide, benzene and oxygen are approximately a factor of two greater in the photo-oxidation experiment; hydrogen and sulfur dioxide are approximately a factor of two lower; carbonyl sulfide is present in nearly the same amount in both experiments. The twentyfold increase in the amount of methane for the photo-oxidation is completely opposite to what one would expect. The situation is the same for benzene, but the difference is much less. The only reasonable explanation is that photo-oxidation takes place rapidly, oxygen is consumed in the early stages, and the process becomes essentially the same as vacuum photolysis except that the predominant gaseous products acts as diluents. In order to explain the sharp increase in

the production of methane, one must assume that photo-oxidation products are able to increase the rate of homolysis and the existing conditions favour the methane forming reactions. The lower amount of SO₂ in the photo-oxidation points to its role as a hydroperoxide decomposer. The fact that water was not isolated in the gaseous oxidation products does not necessarily mean that the SO₂ catalyzed decomposition of hydroperoxide proceeds by a concerted mechanism. It is true that if hydroperoxide decomposition leads to free hydroxyl radicals. Subsequent reactions should lead to the formation of water. However, water could be consumed by the reactive sulfur compounds Eqn. (1.14 – 1.17) and escape detection. Polymer hydroperoxides would decompose in the presence of sulfur dioxide to peroxides and / or esters of sulphuric acid Eqn. (1.14 – 1.17).

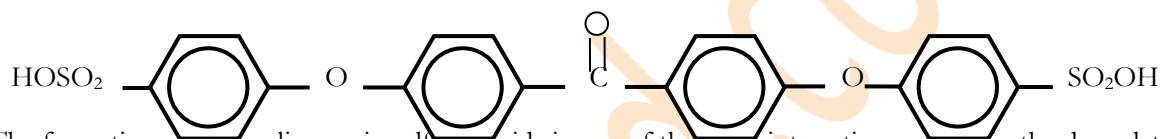


The qualitative identification of sulphate on photo-oxidised polymer surface supports this mechanism.

During the first 12 hours, light exposure causes little change in tensile break strength and modulus but reduces the elongation (Fig.1.18 – 1.21) to 9% of its original value. Further exposure causes no additional change. The intrinsic viscosities of the sole fractions parallel this behavior, showing a reduction of 25% after 12 hours with no subsequent formed during 84 hours of photo-oxidation is nearly 1%, chain scission must be the predominant derivative process. Cross linking is not observed. Elemental analysis (Table A.2) reveals, understandably, that the polymer combines with oxygen on I.

irradiation. Fractionation shows quite surprisingly that the combined oxygen is present only in the polar extract. Furthermore, examination of the sole fractions by infrared analysis discloses that the groups in the total polymer which absorb strongly in the hydroxyl and carbonyl regions are no longer present but appear only in the polar extract.

The solubility behavior of the polar extract coupled with its infrared spectrum and relatively high oxygen and sulfur contents lead to the conclusion that the polar extracts of low molecular weight highly oxidized sulphonic acids. Carbon and sulfur analysis indicate that the polar extract consists mainly of disulfonic acids of type

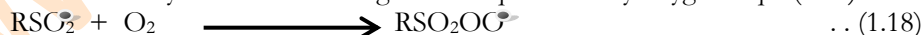


The formation of these oligomeric sulfonic acids is one of the most interesting reactions in the degradative scheme. The experimental evaluation indicates that these compounds play a –

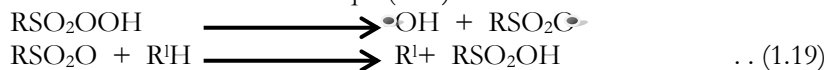
Table A.2 Elemental analysis of irradiated APS films.

	<i>Analysis</i>			
	C%	H%	O%	S%
Calculated total polymer	73.28	5.01	14.46	7.25
72 hours	71.20	4.91	17.00	6.39
Sol Fraction				
60 hours	73.03	4.99	14.84	7.14
72 hours	73.19	5.15	14.68	6.98
84 hours	72.89	5.11	14.96	7.04

– Significant role in the photo-oxidative process. Two pathways are open for the formation of these acids. The sulfonyl radicals formed by C–S bond cleavage can be quenched by oxygen Eqn. (1.18).



Attack of the peroxy radical on polymer on polymer would lead to hydroperoxide. Decomposition of this hydro peroxide would end in a sulfonic acid Eqn. (1.19).



Since in this process a secondary cleavage would be necessary to give rise to disulfonic acids, the large amount of polar extract must arise by an



alternate pathway, depending on the direct decomposition of hydroperoxides by polymer sulfone group Eqn. (1.20).

A similar reaction was reported by Denison and Condit where hydroperoxidized hydrocarbon were the substrate and their decomposition, induced by aliphatic sulfones, lead to sulfonic acids. Elemental analysis of polar extract and sole (Table 3.22) show that the bulk of oxidation is localized in the low molecular weight fragments. It seems reasonable to assume that reactions leading to these fragments or reactions of the fragments themselves are responsible for retarding the oxidative break down of the remaining polymer.

Copper and its compounds are known to act as catalysts for the degradation of polymer. For example, copper pathaloxamine has been found to be an effective catalyst for the oxidation of cumene and related compounds copper is particularly active as a catalyst for the oxidation of natural rubber, GR-S rubber, petroleum products such as gasoline and a whole host of other branched organic polymers.

The catalytic effect of Cu_2O on the photodegradation of APS is drastic in the absence of



Regeneration of RCH_2OOH is suppressed by synergists which reduces $RCH_2OO\cdot$ to $RCH_2O\cdot$, Eqn. (1.21).



RCH_2OOH is removed by non-radical processes which can be followed by reduction of two electrons by thiobiurets and thiourea.

Thus these stabilizers are employed to serve to apparent synergistic functions. The first one is the reduction of $RCH_2OO\cdot$ radical by a two electron process and subsequent inhibition produces alcohol.

In order to confirm the mechanism of substance, the UV spectra of degraded APS samples with and without the stabilizers and Cu_2O have been studied. In the Fig. (3.26 – 3.29) the wavelength which is intense and primarily responsible for the degradation of APS is thought to be ca. 265 and this is connected with carbonyl groups which are present in the degraded polymer. The UV absorption of irradiated neat APS film at ca. 265nm gradually increases with time of irradiation. However, for APS film containing Cu_2O , the increase of the spectral peak is faster than for pure APS, on the other hand, for the polymer containing the stabilizers, the increase at

the stabilizers as it is in their presence. However, it can be seen that degradation becomes catalytic when Cu_2O is present. Without Cu_2O photodegradation of APS proceeds normally and auto catalytically. In the presence of Cu_2O , the degradation reaction rapidly attains a catalytic, and accelerating rate after a shorter “induction period”. The studies of stabilized polymer in the presence and absence of Cu_2O show that induction periods are very regular.

The stabilization against photo-oxidative degradation involves :-

- a) Inhibition of the propagation reaction of $RCH_2OO\cdot$.
- b) Suppression of regeneration of RCH_2OOH , and
- c) Removal of RCH_2OOH through non-radical processes.

The inhibition is also effected by the scavenging of $RCH_2OO\cdot$ radicals with primary antioxidant AH Eqn. (3.10.21).

ca. 265nm is slower than that for the pure APS sample.

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