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Oxidative Degradation of Poly(vinyl Chloride)

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Synopsis

Rates of oxygen consumption and formation of oxidation products were determined in γ-initiated oxidation of poly(vinyl chloride) (PVC) at 25°C. Data are given for five dose rates and correlated on the basis that the overall oxidation is the sum of two reactions that are first order and half order in rate of initiation. The principle oxidation product is hydroperoxide, formed by the half-order reaction, whereas alcohol and carbonyl compounds result mostly from first-order reactions. These products account for 77–80% of the total oxygen absorption. The presence of oxygen was found to increase twofold the rate of dehydrochlorination of irradiated PVC. A reaction scheme is developed which assumes that a significant fraction of the interactions of tertiary peroxy radicals is nonterminating and yields alkoxy radicals which propagate or decompose by β-scission. This decomposition occurs mostly by splitting off a chlorine atom with formation of a ketone and, to a lesser extent, by C—C cleavage which accounts for the observed decrease in molecular weight of the oxidized PVC. Polystyrene was found to be much more resistant to oxidation than PVC. A classification of some commercial polymers in function of their susceptibility to oxidation is proposed.

INTRODUCTION

Thermal degradation of poly(vinyl chloride) (PVC) has been extensively studied in these past years[1–4] while oxidative degradation at ambient temperatures, although of practical importance, has received much less attention.[5,6] Since radiolysis permits the initiation of reactions at room temperature without destroying the important oxidation products, e.g., hydroperoxides and carbonyl groups, its study may be helpful in elucidating the mechanism of the oxidative degradation in polymers and may thus teach us how to accelerate or retard the aging of polymers. We investigated recently the radiation-induced oxidation of polyethylene (PE),[7] polypropylene (PP),[8] and poly(ethylene oxide) (PEO)[9] at ambient temperatures in the dark. We now report a similar study carried out on bulk PVC at 25°C.

Dehydrochlorination, discoloration and formation of free radicals are characteristics of both thermal and radiolytic decomposition of PVC. Polyene chains with long sequences are formed as a result of dehydrochlorination and produce intense color in PVC irradiated *in vacuo*.[10] Degradation under oxygen causes a much lighter discoloration, apparently because the formation of long polyene sequences is hindered by oxidative attacks on the conjugated double bond sys-

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tem.[11] The radicals formed by γ-irradiation react rapidly with the oxygen to give peroxy radicals which lead ultimately to the formation of carbonyl and hydroxyl groups.[12,13] In a detailed study on the radiation-induced oxidation of PVC, Zeppenfeld et al.[14,15] investigated the kinetics of peroxy radical and hydroperoxide formation and concluded that hydroperoxide, hydrogen chloride, and chain scission result from reactions that are first order in rate of initiation. The enhanced thermal instability of PVC irradiated in oxygen is consistent with the generation of labile peroxides.[16]

Although some data on the oxidation products of PVC are available, no quantitative investigation has been reported so far on the oxygen consumption and the relative content of the individual oxygen-containing structures. In this paper, we report our first results on the kinetics of O_2 consumption and of products formation and suggest a mechanism for the radiation-induced oxidation of PVC in the dark at 25°C.

EXPERIMENTAL

Polymer

The polymer used in our experiments was an unstabilized commercial material Solvic 229 from Solvay synthesized by suspension polymerization at 60°C, with number- and weight-average molecular weights of 39,000 and 83,000, respectively, as determined by osmometry and light scattering. The polymer samples were washed several times with water, then with methanol, and finally dried *in vacuo* at 30°C for two days.

Irradiation

Approximately 1 g of the PVC powder (~100 μ resin beads) was introduced in a Pyrex tube and degassed at 10^{-6} torr for 3 hr. A known amount of pure oxygen was then added to give an initial pressure of 680 torr at room temperature. Sealed tubes were then exposed at 25°C in the dark to the γ-rays of a ^{60}cobalt source for various times up to 150 hr at dose rates ranging from 222 to 2740 rad/min (100 rad = 1 gray = 1 J/kg). Dose rates were determined with a Fricke dosimeter taking $G(Fe^{3+})$ as 15.5 ions per 100 eV.

Gas Analysis

After irradiation, the reactor was connected to a vacuum system and cooled to −196°C. The breakseal located on the side arm of the reactor was then opened and noncondensable gases were pumped off from the frozen reactor by a Toeppler pump and measured in a gas buret. Removal of oxygen in a Cu–CuO furnace showed small amounts of hydrogen as water and of carbon monoxide as CO_2. The oxygen consumed by the polymer, ΔO_2, was determined by difference between the initial and final amounts of oxygen. The reactor was then introduced in a Dry Ice bath and the gases evolved (HCl, CO_2, . . .) were removed by the Toeppler pump and measured in the gas buret. These gases were then absorbed in water; gravimetric titrations of the hydrochloric acid by 0.01*N* NaOH showed that they consist entirely of hydrogen chloride and that no significant amounts

of CO_2 are evolved in γ-oxidation of PVC, in contrast with PVC photo-oxidation where CO_2 was found to be one of the major gaseous products.[6] The reactor was finally allowed to warm up to room temperature and the volatile products evolved were pumped off; they consist partly of water and represent between 13% and 24% by volume of ΔO_2, depending on dose rate.

Determination of Functional Groups

Hydroperoxide groups were determined quantitatively by iodometric titration of a 1,2-dichloroethane solution of about 50 mg PVC according to the Mair and Graupner Method I,[17] with a 10-min reflux; the apparent peroxide content did not increase appreciably with longer refluxing time.

Infrared spectroscopy investigations were carried out on 10% solutions of PVC in tetrahydrofuran or on 5% solutions in 1,2-dichloroethane in a 0.05-cm cell. Oxidized PVC exhibits new bands at 1733 and 3550 cm^{-1}. The carbonyl band can be attributed to the absorption of carboxylic acids, aldehydes, ketones, and chloroketones. In order to determine the carboxylic acid content, oxidized PVC was treated by NH_3 gas during 1 hr. As a result, the absorption at 1733 cm^{-1} was reduced to about ⅔ of its original value. The difference between the 1733 cm^{-1} absorptions of untreated and NH_3 treated PVC was used to calculate the carboxylic acid content by taking 4-heptanone and butyric acid as standards. The broad hydroxyl band centered on 3550 cm^{-1} has an absorption which is somewhat larger than expected on the basis of the hydroperoxide content; this suggests that some alcohol groups are also produced in oxidation of PVC. The amount of alcohol was estimated by subtracting from the absorption of the peak at 3550 cm^{-1} the corresponding absorption of hydroperoxide, t-BuO_2H and t-BuOH being used as standards. The weak absorptions of these compounds at low concentrations make this determination of alcohol the least accurate of our determinations.

Determination of Random Chain Scission

Viscosity measurements were carried out at 25°C on dilute solutions of PVC in freshly distilled tetrahydrofuran. The values of the intrinsic viscosity $[\eta]$, before and after degradation, were calculated by one-point measurement by using the Huggins equation[18] in the expanded and appropriate form:

$$[\eta] = [(1 + 4k\eta_{sp})^{1/2} - 1]/2kc$$

where $k = 0.415$ and c is expressed in g PVC/100 cm^3 solvent ($c \leq 1\%$). Number-average molecular weights $\overline{M}_n$ were calculated from intrinsic viscosity by the Mark-Houwink relation[19,20]

$$[\eta](\text{ml/g}) = 2.4 \times 10^{-2}\overline{M}_n{}^{0.77}$$

The average number of chain scissions S per initial macromolecule was then calculated from the relation

$$S = (\overline{M}_{n0}/\overline{M}_n) - 1$$

where $\overline{M}_{n0}$ and $\overline{M}_n$ are the number-average molecular weights of PVC before and after degradation, respectively. This equation is based on the assumptions

TABLE I
Rates of Oxidation R and Radiation Yields G in γ-Initiated Oxidations of PVC at 25°C[a]

	Dose rate 222 rad/min	Dose rate 435 rad/min	Dose rate 720 rad/min	Dose rate 1380 rad/min	Dose rate 2740 rad/min
ΔO_2					
R	7.9	13	18.9	31	52.5
G	57.3	48	42.2	36	30.8
HCl					
R	3.7	6.5	10.5	18.2	35
G	27	24	23.5	21.2	20.5
POOH					
R	3.1 (39.2)[b]	4.5 (34.6)[b]	6.0 (31.8)[b]	8.8 (28.4)[b]	12.6 (24)[b]
G	22.5	16.6	13.4	10.2	7.4
POH					
R	2.3 (14.5)	4.3 (16.7)	7 (18.5)	12.8 (20.8)	25.5 (24.3)
G	16.6	16	15.6	15	15
$>C=O$					
R	2.2 (14)	4.1 (15.8)	6.3 (16.6)	10.3 (16.7)	20 (19.1)
G	15.9	15.2	14	12.0	11.8

$R-C\begin{smallmatrix}\nearrow O \\ \searrow OH\end{smallmatrix}$					
R	0.55 (7)	1.0 (7.7)	1.5 (8)	2.6 (8.3)	5 (9.7)
G	4.0	3.7	3.4	3.0	3.0
CO					
R	0.35 (2.1)	0.7 (2.7)	1.1 (2.8)	1.9 (3)	3.7 (3.5)
G	2.5	2.6	2.4	2.2	2.2
Volatile products					
R	1.9	2.7	3.6	4.7	6.5
G	14	10	8	5.5	3.8
Scission					
R	0.45	0.84	1.2	2.1	3.8
G	3.3	3.1	2.6	2.3	2.2
ΔO_2 Calculated[c]					
R	6.07	10.05	14.7	23.9	42.2
G	44.0	37.2	32.8	27.8	24.9
$\frac{\Delta O_2 \text{ calcd}}{\Delta O_2 \text{ obsd}}$ %	76.8	77.5	77.7	77.2	80.6

[a] Rates are in 10^{-4} mole/kg PVC-hr.

[b] Each number in parentheses is the per cent of O_2 accounted for by the indicated product.

[c] G_{O_2} calc. $= G_{POOH} + G_{R-C\begin{smallmatrix}\nearrow O \\ \searrow OH\end{smallmatrix}} + \frac{1}{2}(G_{POH} + G_{>C=O} + G_{CO})$.

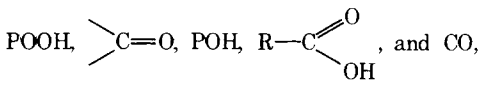
that chain fracture is a random process, that no intermolecular crosslinking occurs, and that the initial molecular weight distribution is random, i.e., $\overline{M}_{w_0} = 2\overline{M}_{n_0}$.

RATES AND PRODUCTS OF OXIDATION OF PVC AT 25°C

Effect of Irradiation Time

PVC samples were exposed to ionizing radiation at 25°C for different times (up to 150 hr) and dose rates, at total doses between 0.9 and 10 Mrad. To ensure that, under our experimental conditions, the oxidation process was not controlled by the rate of diffusion of oxygen into the polymer, γ-irradiations of PVC were carried out for 100 hr at various initial O_2 pressures: 280, 390, 550, and 680 torr. The observed oxygen consumption was the same, within experimental errors, in the four experiments, i.e., the rate of oxidation was not O_2-diffusion controlled. Further experiments were always carried out in the presence of excess oxygen (p_{O_2} = 680 torr).

The amount of oxygen consumed by the polymer irradiated at a given dose rate increases linearly with the irradiation time over the whole range of doses investigated; the various functional groups resulting from the oxidation of PVC,



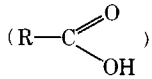
also accumulate linearly without any detectable induction period. Figure 1 shows, as an example, the results of four experiments carried out at a dose rate of 435 rad/min. The values of the rates R of oxygen consumption and of products formation were determined from the slope of the straight lines for each of the five dose rates investigated. Results are shown in Table I. Values of the corresponding radiochemical yields G, i.e., the number of molecules of oxygen consumed or of products formed per 100 eV absorbed by the polymer, were calculated from the relation

$$G = 9.65 \times 10^8 R/I$$

when R is expressed in mole/kg PVC-hr, and the absorbed dose rate I, in rad/hr.

Oxygen Balance

The main oxidation product is hydroperoxide (POOH) which accounts for 39% of the oxygen uptake at the lowest dose rate and for 24% at the highest. Post-irradiation investigations on oxidized PVC reveal this hydroperoxide to be stable at room temperature; no appreciable change of the POOH content of the irradiated polymer could be noticed after two weeks of storage at 25°C in the dark. This result is in agreement with the observations of Zeppenfeld and Wuckel[15] and corroborates the observed linear increase of hydroperoxide with irradiation time (Fig. 1). Aldehyde + ketone (>C=O) and alcohol groups (POH) are formed at similar rates and account each for about 14% to 20% of O_2 uptake, depending on dose rate, whereas carboxylic acid



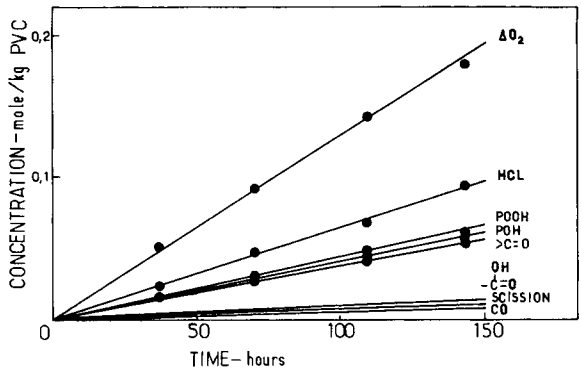


Fig. 1. Oxygen uptake and oxidation products as a function of irradiation time in oxidations of PVC at 25°C. Dose rate = 435 rad/min.

and carbon monoxide account for an additional ~8% and 3%, respectively, of ΔO_2. The yield of oxygen incorporated in the oxidation products of PVC can then be determined from the following equation:

$$G_{O_2\text{calculated}} = G_{\text{POOH}} + G_{\text{R}-\underset{\underset{\text{OH}}{|}}{\text{C}}=\text{O}} + \frac{1}{2}[G_{\text{POH}} + G_{>\text{C}=\text{O}} + G_{\text{CO}}]$$

Values of G_{O_2} calculated are given in Table I. Comparison with the observed G_{O_2} values shows that these oxidation products account for approximately 77–80% of the oxygen consumed. The missing oxygen in our material balance is expected to be in some dialkyl peroxides and in the volatile products which represent 13–24% by volume of the oxygen uptake.

Dehydrochlorination

When PVC is irradiated in the presence of oxygen, large amounts of hydrogen chloride are evolved. Our technique of gas analysis allows us to determine accurately the yield of HCl formation in comparison with the yield of oxygen consumption. It appears that ~0.5 to 0.66 molecule of hydrogen chloride is formed for each molecule of O_2 consumed, depending on dose rate. The degree of dehydrochlorination or the conversion, defined as the ratio of hydrogen chloride evolved to the totally available amount, increases linearly with the irradiation time (Fig. 1). Under our experimental conditions, the rate of dehydrochlorination (0.0023%/hr $< r <$ 0.022%/hr) is, however, relatively low compared with thermal degradation of PVC in oxygen (r = 0.6%/hr at 180°C).[21] When irradiations of PVC are carried out *in vacuo* at 25°C, the radiation yield of dehydrochlorination ($G_{\text{HCl}} = 12.8$) is about half as large as the yield observed in experiments carried out in the presence of oxygen ($20 < G_{\text{HCl}} < 27$). This is in agreement with the known effect of oxygen which accelerates dehydrochlorination of thermally degraded PVC.[1,21]

Change in Molecular Weight

The intrinsic viscosity and the calculated molecular weight of radiation oxidized PVC decrease slightly with irradiation time, in agreement with previous

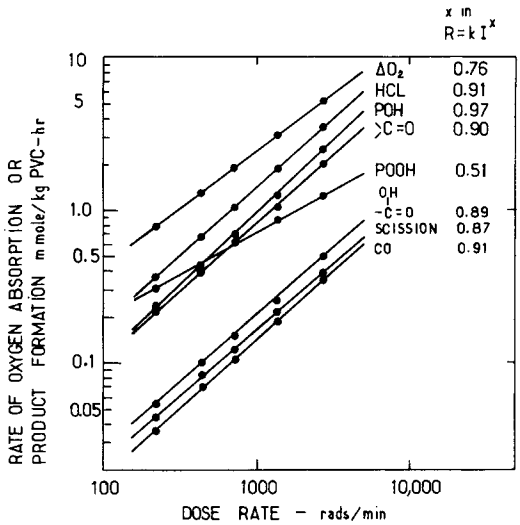


Fig. 2. Rates of oxygen consumption or product formation as a function of dose rate in oxidations of PVC at 25°C.

observations.[5,13] The radiochemical yield of net chain scission increases moderately with decreasing dose rate ($2.2 < G_{\text{scission}} < 3.3$) but remains always inferior to the yield of carboxylic acid:

$$3 < G_{\mathrm{R}-\underset{\underset{\mathrm{OH}}{|}}{\mathrm{C}}=\mathrm{O}} < 4$$

However, if simultaneous scission and crosslinking occur, as suggested by Salovey et al.,[13] the true value for G_{scission} will become somewhat larger and may exceed

$$G_{\mathrm{R}-\mathrm{C}\overset{\mathrm{O}}{\underset{\mathrm{OH}}{\diagup\diagdown}}}$$

It should be mentioned that our value of G_{scission} is much lower than the value determined by Zeppenfeld and Wuckel[15] ($G_{\text{scission}} = 23$), although both investigations were carried out under similar experimental conditions.

Effect of Dose Rate

To determine the kinetic order of the reactions involved in the oxidation process of PVC, we carried out irradiations at five dose rates: 222, 435, 720, 1380, and 2740 rad/min. When the rates R of O_2 consumption and formation of oxidation products are plotted as functions of the dose rate I on logarithmic scales (Fig. 2), the relation obtained has the form

$$R = kI^x$$

where the exponent x for each product lies between 0.5 and 1. The formations of HCl, POH,

$$>\mathrm{C}=\mathrm{O},\ \mathrm{R}-\mathrm{C}\overset{\mathrm{O}}{\underset{\mathrm{OH}}{\diagup\diagdown}},\ \mathrm{CO},$$

and chain scissions are nearly first order in rate of initiation ($0.87 < x < 0.97$), whereas the rate of formation of hydroperoxides is half order in rate of initiation. The rate of oxygen consumption is intermediate ($x = 0.76$) and is assumed to be the sum of two reactions that are first order and half order in rate of initiation. The radiochemical yield for oxygen consumption increases from 30.8 to 57.3 with decreasing dose rate, in the range of dose rates investigated. These relatively high values of G_{O_2} are consistent with a chain reaction process; they are about the same as the values of G_{O_2} that we measured in γ-initiated oxidations at 22°C of atactic polypropylene:[8] $30 < G_{O_2} < 80$ in the same range of dose rates.

MECHANISM OF OXIDATION OF PVC

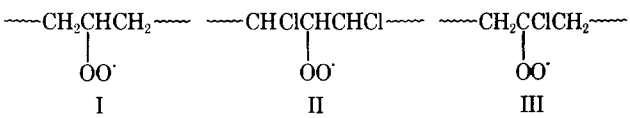
Radicals in PVC

ESR investigations[22] on PVC irradiated *in vacuo* at low temperatures have shown that alkyl radicals arise from carbon–chlorine and carbon–hydrogen bond scissions. As the irradiated polymer is allowed to warm to room temperature, these radicals are replaced by polyenyl radicals resulting from the evolution of hydrogen chloride by alkyl radicals:[23,24]

$$\sim\!CH_2\text{—}\dot{C}H\text{—}CH_2\text{—}CHCl\sim \rightarrow (CH{=}CH)_n\dot{C}H\text{—}CH_2\text{—}CHCl\sim + nHCl$$

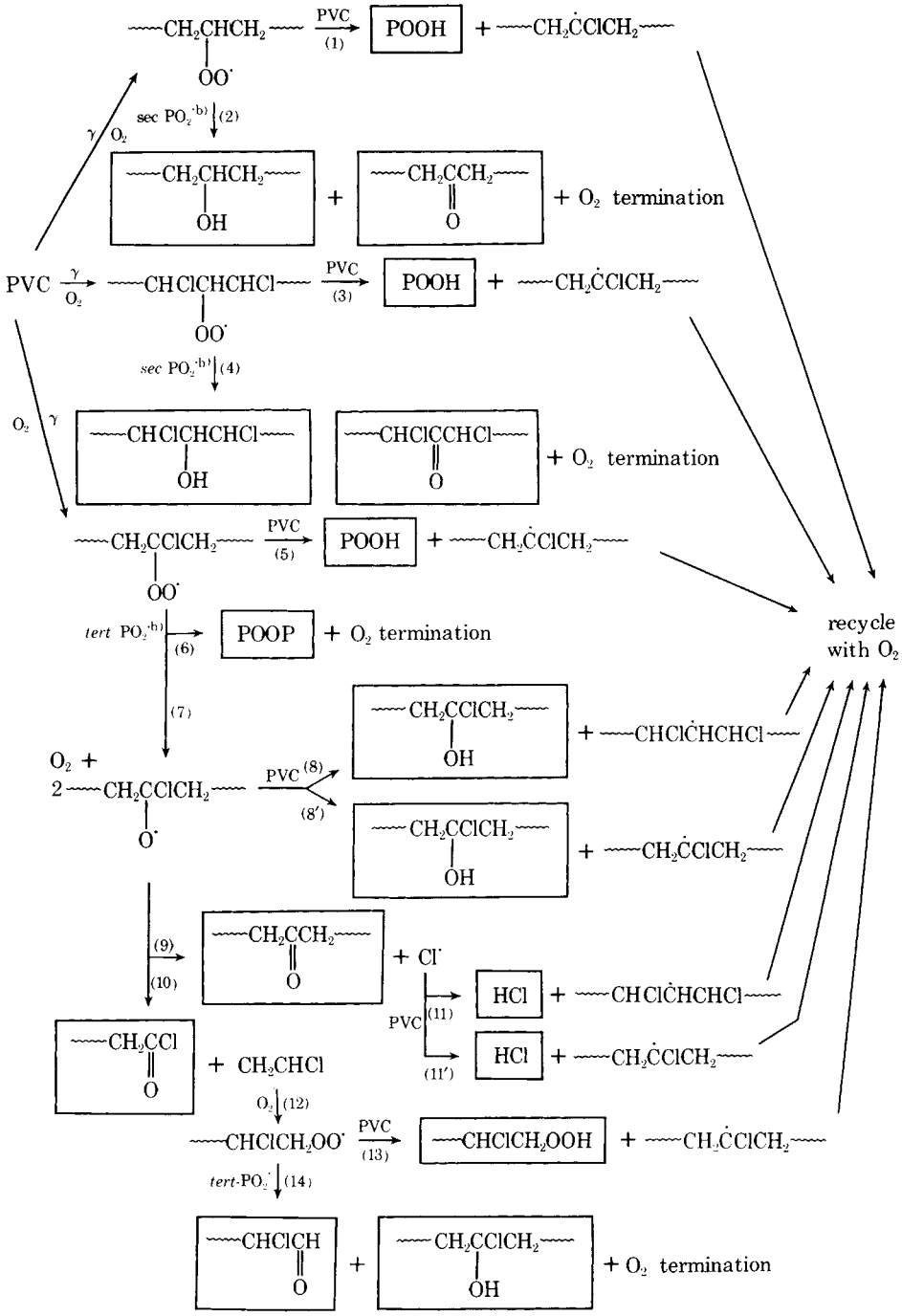
Even though the alkyl radicals are expected to react with O_2 when irradiations are carried out in the presence of oxygen, the above-mentioned reaction may still proceed since the chlorine atom split off from the PVC chain is kinetically excited and readily abstracts a neighboring hydrogen atom. The resulting polyenyl structure which is responsible for color formation in PVC irradiated *in vacuo* was shown to be rapidly destroyed by oxidative attack;[23,24] indeed, no discoloration of the oxidized polymer could be noticed, even for the most degraded of our samples.

Thus, in the presence of an adequate supply of oxygen, the main initiating species in γ-oxidation of PVC are expected to be the secondary and tertiary peroxy $PO_2^{\cdot}$ radicals resulting from addition of an oxygen molecule on the three kinds of alkyl radicals formed by C—Cl and C—H bond scissions:



Salovey and Gebauer[13] suggested recently a mechanism for the radiolysis of PVC in air which involves the reactions of radical I, but made no mention of radicals II and III. Since radical I does not arise from the attack of the polymer by peroxy radicals but mainly from the direct effect of the ionizing radiation and since our results show that propagation reactions play a significant part in the oxidation process, we expect the predominant routes to involve species' II and III rather than species I. Furthermore, the propagation reactions by peroxy radicals should generate mostly radical III since a tertiary C—H bond is about 25 times more reactive than a secondary C—H bond toward alkylperoxy radicals at 25°C,[25] so that the main oxidation products of PVC are assumed to result principally from the reaction of the α-chloroalkyl peroxy radical III.

SCHEME A
γ-Oxidation of Poly(vinyl chloride)[a]



[a] Final products are in boxes.
[b] Cross termination by the various types of $PO_2^{\cdot}$ radicals are also possible.

Reaction Scheme

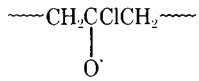
The reactions of radicals I, II, and III, expected from the work on model compounds,[26] have been represented in Scheme A. They appear to account satisfactorily for the major products observed in radiation-induced oxidations of PVC at 25°C.

Reactions of Secondary $PO_2^{\cdot}$ Radicals

The secondary peroxy radicals I and II can abstract the labile hydrogen atoms from an adjacent chain to form hydroperoxide groups and chain carrier backbone radicals, mostly tertiary ones, reactions (1) and (3). Since hydroperoxide of PVC was found to be quite stable at room temperature, we conclude that the observed degradation of the polymer does not result from the decomposition of POOH group. The other route for disappearance of secondary peroxy radicals is the terminating bimolecular self-reaction which, according to the Russell mechanism,[27] leads to a ketone and a secondary alcohol, reactions (2) and (4). Cross terminations of secondary and tertiary $PO_2^{\cdot}$ radicals may also take place to yield ketones and tertiary alcohols.

Reactions of Tertiary $PO_2^{\cdot}$ Radicals

Besides reacting with the polymer to give hydroperoxides, reaction (5), tertiary peroxy radicals III may also disappear either by terminating interactions with formation of dialkyl peroxides, reaction (6), or by nonterminating interactions to yield free alkoxy radicals, reaction (7). To account for the large yields of alcohol and carbonyl compounds formed in reactions that are first order in rate of initiation, we assume that a significant fraction of tertiary $PO_2^{\cdot}$ radicals interactions are nonterminating. This assumption is consistent with our previous observations[8] on γ-initiated oxidations of atactic polypropylene which suggest that about half of the interactions of tertiary peroxy radicals are nonterminating at ambient temperatures and yield alkoxy radicals which propagate or decompose. The principal fate of the tertiary alkoxy radical

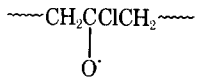


evolved in reaction (7) is either the hydrogen abstraction from the polymer to yield an alcohol and a chain carrier secondary or tertiary alkyl radical, reactions (8) and (8′), or the decomposition by β-scission[29] which may occur either by cleavage of the C—Cl bond, reaction (9) or by C—C cleavage, reaction (10). (Some secondary alkyl radicals ~~CHCl—$\dot{C}$H—CHCl~~ are likely to be formed by propagation since alkoxy radicals are much less selective than peroxy radicals for hydrogen abstraction and exhibit approximately the same reactivity towards secondary or tertiary hydrogen.[28])

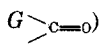
Reaction (9), which yields a ketone and a chlorine atom, may account for the relatively high carbonyl group content observed on the oxidized polymer. This reaction may also explain why the radiation-induced dehydrochlorination of PVC is about twice faster in oxygen than *in vacuo*. In both cases, hydrogen chloride will result primarily from the direct cleavage of the C—Cl bond by radiation, but

in the presence of oxygen, additional amounts of HCl may be formed in the attack of the polymer by the chlorine atom evolved in reaction (9), with formation of a propagating secondary or tertiary alkyl radical, reactions (11) and (11′). According to Miller[11] and Winkler,[29] the chlorine atom will react mostly by abstraction of a methylene hydrogen to form a secondary alkyl radical, i.e., reaction (11) is preferred over reaction (11′).

If decomposition of the alkoxy radical



occurs by C—C cleavage, reaction (10), it will induce the scission of the polymer chain with formation of an α-chloroketone group and of a primary alkyl radical which will react with oxygen, reaction (12). The primary peroxy radical evolved is then expected to disappear mostly by terminating interaction with another $PO_2^{\cdot}$ radical, reaction (14), rather than by propagation, reaction (13), because primary peroxy radicals are about 10^3 to 10^4 times more reactive than tertiary peroxy radicals in chain termination in small hydrocarbons.[30] The relatively low values of the yield in main chain scission (about one fifth of



suggest that reaction (9) is favored over reaction (10), i.e., the tertiary alkoxy radical from reaction (7) will decompose preferentially by splitting off a chlorine atom.

It finally remains to account for the formation of the two minor oxidation products of PVC, carboxylic acid and carbon monoxide. We assume that carboxylic acids result principally from the rapid oxidation of the aldehyde groups produced in the termination reaction (14). Concerning the formation of the small amounts of carbon monoxide, the most likely reaction would be the decarbonylation of some of the α-chloroketone generated in reaction (10); an other possibility is the loss of CO from oxidizing aldehyde.

Kinetics

It should be mentioned that reaction Scheme A presents a close analogy with the scheme that was developped previously for the oxidation of polypropylene.[8,31] Kinetic calculations based on scheme A lead, therefore, to an equation for the steady rate of oxygen consumption in PVC oxidation which is very similar to the equation derived for polypropylene:[31]

$$-dO_2/dt = R_{O_2} = (0.5 + p)R_i + [k_p/(2k_t)^{1/2}][\mathrm{PVC}]R_i^{1/2} \qquad \text{(B)}$$

where R_i is the rate of production of initiating radicals and k_p and k_t are the rate constants of propagation and termination, respectively, by $PO_2^{\cdot}$ radicals. The first term on the right-hand side of eq. (B) refers to the oxygen consumed in reactions that are first order in rate of initiation: one half molecule of O_2 is consumed per initiating radical in initiation and termination, and p additional molecules of O_2 are consumed in first-order propagation reactions which yield alcohol groups and cleavage products of alkoxy radicals. The last term in eq. (B) is the oxygen uptake associated with formation of hydroperoxides that is half

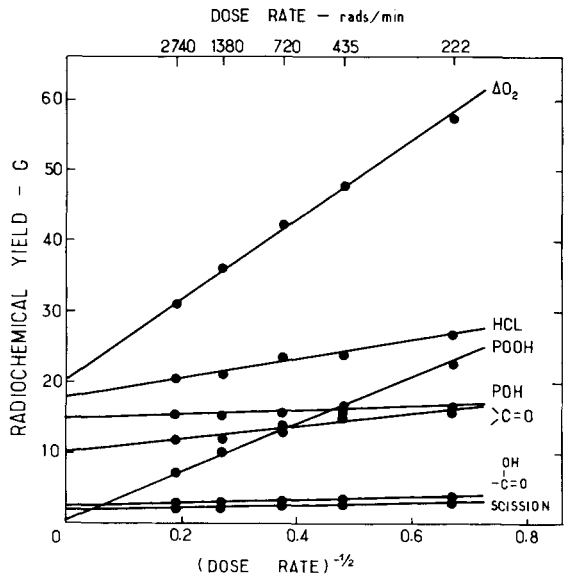


Fig. 3. Radiochemical yields G as a function of (dose rate)$^{-1/2}$ in oxidations of PVC at 25°C.

order in rate of initiation. Since the radiochemical yield for O_2 consumption is proportional to the ratio of rate of oxidation to dose rate, $G_{O_2} = KR_{O_2}/I$, the kinetic law can be written as

$$G_{O_2} = \alpha_{O_2} + \beta_{O_2} I^{-1/2} \tag{C}$$

where

$$\alpha_{O_2} = K(0.5 + p)R_i/I \text{ and } \beta_{O_2} = (KG_i/2k_t)^{1/2} k_p [\text{PVC}]$$

with $K = 9.65 \times 10^8$ mole^{-1} kg rad, G_i representing the yield of initiating radicals.

Correlation with Experimental Data

According to relation (C), the radiochemical yield of oxygen consumption is a linear function of (dose rate)$^{-1/2}$. Figure 3 shows that plots of G values for O_2 uptake and products against (dose rate)$^{-1/2}$ are indeed straight lines. The intercept α is the radiochemical yield of O_2 consumed or of products formed in reactions that are first order in rate of initiation; the slope β is the radiochemical yield of O_2 consumed or of products formed at unit rate of initiation in half-order reactions. Thus, the term α for hydroperoxide should be zero, which is confirmed experimentally, while the term β should be zero for POH and

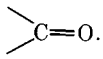


Figure 3 shows that the formation of alcohol is nearly first order in rate of initiation, as expected, whereas the carbonyl compounds result from both first-order and half-order reactions. Our best present explanation for the half-order component of

is that a fraction of the primary peroxy radicals ~CHClCH$_2$OO· propagate by reaction (13) instead of terminating, with formation of alkyl radicals which lead, after peroxidation, to the production of ketone groups that are associated with half-order chain propagation.

COMPARISON OF THE OXIDIZABILITY OF SOME COMMERCIAL POLYMERS

The best measure of the relative overall reactivity of a polymer in oxidation is its rate of oxygen consumption at known rate of initiation. In our recent investigations on the radiation-induced oxidation of some solid polymers (PE,[7] PP,[8] PEO[9]), we determined the rate of O_2 uptake for different dose rates. In addition to the foregoing investigation on PVC, we also carried out some oxidation experiments on solid polystyrene that we now briefly describe.

Radiation-Induced Oxidation of Polystyrene at 25°C

The polymer used in our experiments was an unstabilized commercial material Gedex from Charbonnage de France Chimie. Polystyrene (PS) samples, in a finely dispersed state, were exposed to ionizing radiation at 25°C in the presence of pure oxygen at dose rates ranging from 800 to 3450 rad/min. Gas analyses were conducted as described previously to determine the amount of oxygen consumed. The rate of O_2 consumption appears to be very low and remains constant with irradiation time in the whole range of doses investigated (5 to 20 Mrad). The overall rate of oxidation is first order in rate of initiation; hence, the radiochemical yield G_{O_2} is independent of dose rate, and its constant value can be estimated to be ~1.0 ± 0.2. The major oxidation product is hydroperoxide

TABLE II
Radiochemical Yields of O_2 Consumption and Kinetic Chain Lengths in γ-Initiated Oxidations at 25°C of Some Commercial Polymers

Polymer	Supplier	Yield of O_2 uptake G_{O_2}: Dose rate 1000 rad/min	Yield of O_2 uptake G_{O_2}: Dose rate 100 rad/min	Order of rate of oxidation x[a]	Yield of initiating radicals G_i[b]	Number of O_2 molecules consumed per initiating radical G_{O_2}/G_i: Dose rate 1000 rad/min	Number of O_2 molecules consumed per initiating radical G_{O_2}/G_i: Dose rate 100 rad/min
PE[c]	Solvay Eltex	11	18	0.85	5.8	1.9	3.1
PS	CdF Chimie Gedex	1	1.1	0.98	0.2	5	5.5
PP[d]	Avisun	45	120	0.56	4.8	9.4	25
PVC	Solvay Solvic	39	70	0.78	2.6	15	27
PEO	Hoechst	175	380	0.66	4.8	36	79

[a] Order x of the rate of oxidation R_{O_2} with initiation rate I: $R_{O_2} = kI^x$.
[b] G values of paramagnetic centers as determined by Kiryukhin and Milinchuk.[33]
[c] Oxidations carried out at 45°C.
[d] Oxidations carried out at 22°C.

which accounts for ~60% of the oxygen uptake. Infrared spectra of the oxidized polymer exhibit small absorptions in the carbonyl region at 1710 cm^{-1}, and in the hydroxyl region between 3400 and 3600 cm^{-1}. Benzaldehyde and acetophenone were detected by GLC analyses on chloroform solution of the oxidized PS; these low molecular weight compounds are minor oxidation products that account for only ~3% each of the oxygen uptake. However, when we irradiated chloroform solutions of PS in air at 25°C, much larger amounts of these two products were observed.[32] Besides, it should be mentioned that PS plasticized with ~3% of chloroform prior to irradiation oxidizes five times faster ($G_{O_2} \simeq 5$) than pure PS, as expected from the decrease of the glass transition temperature and the resulting increased mobility of the radicals which favors chain peroxidation.

Radiochemical Yields of Oxygen Consumption in Some Polymers

To test the relative ability of some commercial polymers to oxidize, we now compare in Table II the respective radiochemical yields of oxygen uptake that we determined by irradiating these polymers in the presence of oxygen. All of the oxidation experiments have been carried out on solid polymers under the same experimental conditions, i.e., γ-irradiation in the dark, at ambient temperature, and in the presence of an excess of pure oxygen so that oxidations were not O_2-diffusion controlled.

The third and fourth columns of Table II list G values of O_2 consumption for the various polymers investigated, at two dose rates chosen arbitrarily at 100 and 1000 rad/min. Depending on G_{O_2}, these polymers can be classed in the following order of increasing sensitivity toward oxidation: PS < PE < PVC < PP < PEO.

The fifth column indicates the order x of the rate of oxidation $R_{O_2} = kI^x$. It appears that all of these polymers oxidize at rates which lie between half and first order in rate of initiation. The above correlating equation permits the calculation of the rate of oxidation for anyone of these polymers at a given dose rate; in the same way, G values for O_2 uptake can be easily determined at any dose rate from a logarithmic plot of G against I, which is a straight line with a negative slope $(x - 1)$.

Even though the G value for O_2 consumption gives a good indication of the extent of the oxidation in each polymer, it is more accurate, for a reliable comparison of the oxidizability of various polymers, to refer to the amount of oxygen consumed per initiating radical since the rate of oxidation will depend primarily on the number of initiating sites created in the polymer by the ionizing radiation. The sixth column of Table II lists the G values of paramagnetic centers reported recently by Kiryukhin and Milinchuk[33] for the considered polymers. In the last two columns, we report the calculated values of the ratio G_{O_2}/G_i, i.e., the number of O_2 molecules consumed per initiating radical, for the two dose rates 100 and 1000 rad/min. By taking G_{O_2}/G_i as a better parameter of the oxidizability than G_{O_2}, the classification becomes the following: PE < PS < PP < PVC < PEO.

Because the rates of oxidation of these polymers are less than first order in rate of initiation, the ratio G_{O_2}/G_i, which reflects the extent of the chain reaction process, will increase with decreasing dose rate. However, Table II shows that this does not affect significantly the proposed classification in the range of dose rates considered. Values of G_{O_2}/G_i show a gradual transition in susceptibility to oxidation from PE and PS which are most resistant through PP and PVC to

PEO, which is most susceptible and about 20 times as reactive as PE. This transition reflects both an increasing reactivity in chain propagation (β values range from 19 $rad^{1/2}$ $sec^{-1/2}$ in PE to 508 $rad^{1/2}$ $sec^{-1/2}$ in PEO) and a decreasing rate of chain termination.

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References

1. W. C. Geddes, *Rubber Chem. Technol.*, **40,** 177 (1967).
2. D. Braun, *Pure Appl. Chem.*, **26,** 173 (1971).
3. Z. Mayer, *J. Macromol. Sci. C*, **10,** 263 (1974).
4. G. Avrey, B. C. Head, and R. C. Poller, *J. Polym. Sci.*. Macromol. Rev., **8,** 1 (1974).
5. A. Chapiro, *Radiation Chemistry of Polymeric Systems,* Wiley-Interscience, New York, 1962.
6. K. P. S. Kwei, *J. Polym. Sci. A1,* **7,** 1075 (1969).
7. C. Decker, F. R. Mayo, and H. Richardson, *J. Polym. Sci. A1,* **11,** 2879 (1973).
8. C. Decker and F. R. Mayo, *J. Polym. Sci. A1,* **11,** 2847 (1973).
9. C. Decker, *J. Polym. Sci.,* in press.
10. G. J. Atchison, *J. Appl. Polym. Sci.,* **7,** 1471 (1963).
11. A. A. Miller, *J. Phys. Chem.*, **63,** 1755 (1959).
12. S. Ohnishi, S. Sugimoto, and I. Nitta, *J. Polym. Sci., A* **1,** 625 (1963).
13. R. Salovey and R. G. Gebauer, *J. Polym. Sci. A1,* **10,** 1533 (1972).
14. G. Zeppenfeld and A. Bartl, *J. Polym. Sci. C,* **11,** 4369 (1969).
15. G. Zeppenfeld and L. Wuckel, *Proceedings of Second Tihany Symposium on Radiation Chemistry,* Dobo and Hedvig, Budapest, 1967, p. 765.
16. R. Salovey and R. G. Badger, *J. Appl. Polym. Sci.,* **16,** 3265 (1972).
17. R. D. Mair and A. J. Graupner, *Anal. Chem.*, **36,** 194 (1964).
18. M. L. Huggins, *J. Amer. Chem. Soc.*, **64,** 2716 (1942).
19. M. Kolinsky, M. Ryska, M. Bohdanecky, P. Kratochvil, D. Solc, and D. Lim, *J. Polym. Sci. C,* **16,** 485 (1967).
20. M. Bohdanecky, K. Solc, P. Kratochvil, M. Kolinsky, M. Ryska, and D. Lim, *J. Polym. Sci. A2,* **5,** 343 (1967).
21. K. B. Abbas and E. M. Sorvik, *J. Appl. Polym. Sci.,* **17,** 3577 (1973).
22. E. J. Lawton and J. S. Balwit, *J. Phys. Chem.*, **65,** 815 (1961).
23. R. Salovey and J. P. Luongo, *J. Polym. Sci. A1,* **8,** 209 (1970).
24. R. Salovey, R. V. Albarino, and J. P. Luongo, *Macromolecules,* **3,** 314 (1970).
25. D. M. Brown and A. Fish, *Proc. Roy. Soc.* (London), **A308,** 547 (1969).
26. N. Grassie, *Chemistry of High Polymer Degradation Processes,* Interscience, New York, 1956.
27. G. A. Russell, *J. Amer. Chem. Soc.*, **79,** 3871 (1957).
28. D. L. Allara and D. Edelson, *Rubber Chem. Technol.*, **45,** 437 (1972).
29. D. E. Winkler, *J. Polym. Sci.*, **35,** 3 (1959).
30. K. U. Ingold, *Accts Chem. Res.*, **2,** 1 (1969).
31. E. Niki, C. Decker, and F. R. Mayo, *J. Polym. Sci. A1,* **11,** 2813 (1973).
32. S. Godard, C. Decker, P. Anton, and J. Marchal, *Makromol. Chem.*, **175,** 441 (1974).
33. V. P. Kiryukhin and V. G. Milinchuk, *J. Polym. Sci. USSR,* **16,** 941 (1975).

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