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Abstract

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ON THE OXIDATIVE DESTRUCTION OF POLYFORMALDEHYDE

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Unlike most polymeric materials, polyformaldehyde (PFA) contains a heteroatom in the main chain and is characterized by a low ceiling temperature (1). It should be expected that these features will affect the course of various processes of polymer destruction, in particular oxidation. Since the PFA molecule contains no side chains, the formation of peroxide groups is possible through the interaction of oxygen with the carbon atoms of the main chain. It is very likely that the presence of an oxygen bridge between the carbon atoms will promote the low stability of peroxide compounds and will make them analytically difficult to determine. The ceiling temperature for PFA is +100° (2); consequently, any process proceeding at higher temperatures will be accompanied by the competing depolymerization reaction. Since oxidation of PFA proceeds at a noticeable rate at temperatures of 160—180° (3), one should expect the reaction products to contain, along with oxygen-containing compounds, considerable amounts of monomer.

We investigated the products of thermo-oxidative destruction of PFA with hydroxyl and acetyl end groups at temperatures of 180—185°. It is quite obvious that at higher temperatures the share of the depolymerization reaction will increase; at the same time, the probability of secondary processes distorting the general picture of oxidation of the polymer itself also increases. The experiments were carried out with oxygen circulating through the polymer melt in a closed system at a pressure close to atmospheric. The condensable products were continuously absorbed immediately after the reactor throughout the entire experiment and were determined chromatographically (4) and chemically (5). The results of the experiments are given in Table 1,

Table 1

Analysis of PFA decomposition products

Polymer characteristic	Decomposition temperature, °C	Degree of conversion, %	CH_2O	HCOOH	H_2	CO_2	CO	C balance, %	H balance, %	Oxygen consumption, mol/mol of absorbed O_2
PFA with hydroxyl end groups $M_\omega = 2.46\cdot 10^5$	180	70.0	86.5	5.3	0.9	2.0	–	94.8	92.7	–
PFA with hydroxyl end groups $M_\omega = 2.46\cdot 10^5$	180	100.0	80.0	8.4	1.2	1.3	3.2	92.9	89.6	–
PFA with hydroxyl end groups $M_\omega = 2.46\cdot 10^5$	180	100.0	81.5	8.7	1.1	2.2	0.4	92.8	91.3	21
PFA with acetyl end groups $M_\omega = 1.64\cdot 10^5$	180	11.0	100.0	8.3	0	1.3	0	109.6	108.3	13

Polymer characteristic	Decomposition temperature, °C	Degree of conversion, %	CH_2O	HCOOH	H_2	CO_2	CO	C balance, %	H balance, %	Oxygen consumption, mol/mol of absorbed O_2
PFA with acetyl end groups $M_\omega = 1.64 \cdot 10^5$	180	35.0	96.0	4.3	0.4	1.2	–	101.5	100.7	11
PFA with acetyl end groups $M_\omega = 1.64 \cdot 10^5$	180	75.0	87.2	4.4	0.6	0.5	–	92.0	92.2	–
PFA with acetyl end groups $M_\omega = 1.64 \cdot 10^5$	185	100.0	80.0	5.6	0.8	1.1	–	86.7	86.4	28

from which it is evident that, irrespective of the nature of the end groups, the principal reaction product is monomeric formaldehyde. Indeed, for every 20 moles of evolved monomeric formaldehyde, on average, one mole of oxygen is absorbed. The elemental balance data indicate

This indicates that, if any products not identified by us are formed in the reaction, their fraction is small. It should be noted that we were unable to detect any peroxide compounds.

On the basis of the experimental data presented, one may conclude that only oxygen-initiated depolymerization of PFA occurs, and that an oxidative direction of the reaction is practically absent. Let us consider how the experimental results agree with known data on the rate constants of elementary oxidation steps for various hydrocarbons.

Oxygen initiates decomposition according to the reaction

$$\sim \mathrm{CH_2 - O - CH_2 - O - CH_2} \sim + \mathrm{O_2} \rightarrow \sim \mathrm{CH_2 - O - \dot{C}H - O - CH_2} \sim + \mathrm{HO_2^{\bullet}} \tag{0}$$

The macroradical formed may either decompose

$$\sim \mathrm{CH_2 - O - \dot{C}H - O - CH_2} \sim \rightarrow \sim \mathrm{CH_2 - O - CH{=}O + \dot{C}H_2} \sim \tag{1}$$

or add an oxygen molecule

$$\sim \mathrm{CH_2 - O - \dot{C}H - O - CH_2} \sim + \mathrm{O_2} \rightarrow \sim \mathrm{CH_2 - O - CH(OO^{\bullet}) - O - CH_2} \sim \tag{1'}$$

Let us estimate the probable rates of each of these processes. Reaction (1) is monomolecular and endothermic by 15 kcal/mole, since in its course the same bonds are broken and formed as in the depolymerization of PFA (6). Consequently, the activation energy of elementary step (1) will be close to 17 kcal/mole, and the rate at 180° will be expressed as

$$W_1 = 10^{13} \cdot 10^{-1700/(4.6 \cdot 453)}[\mathrm{R}],$$

where [R] is the concentration of active centers.

The addition of oxygen (reaction $(1')$) is a bimolecular process proceeding with an activation energy of 2-3 kcal/mole and a steric factor $f = 10^{-4}$–10^{-5} (7); its rate will be expressed by the equation

$$W_{1'} = 3.5 \cdot 10^{-17}[\mathrm{R}][\mathrm{O_2}].$$

The concentration of oxygen in the polymer melt under the conditions of our experiments ($P_{\mathrm{O_2}}$ close to 760 mm Hg and $T = 180°$) may be estimated as $3 \cdot 10^{19}$ molecules/cm^3.

Comparing W_1 and $W_{1'}$, it is easy to see that reaction (1) proceeds at a rate 1-2 orders of magnitude higher than the rate of $(1')$.

In an analogous way, the radical formed in reaction (1) eliminates monomer 10-100 times faster

$$\sim \mathrm{CH_2 - O - CH_2 - O - \dot{C}H_2} \rightarrow \sim \mathrm{CH_2 - O - \dot{C}H_2 + O{=}CH_2} \tag{2}$$

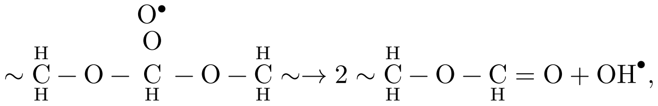
than it forms a peroxide radical according to the reaction

$$\sim CH_2 - O - CH_2 - O - \dot{C}H_2 - O_2 \rightarrow \sim CH_2 - O - CH_2 - O - CH_2 - OO^\bullet \qquad (2')$$

Indeed, in reaction (2) the same bonds are broken and formed as in process (1), and it is monomolecular, whereas reaction (2′) is nothing other than the oxygen addition to a radical considered above.

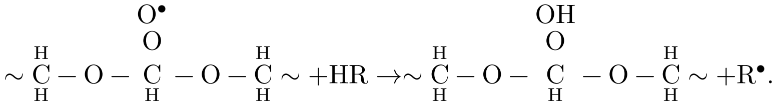
Thus, the results of the calculation agree well with experiment. Despite the fact that the rate of formation of the peroxide radical, as follows from the calculation, is 10-100 times lower than the rate of its monomolecular transformations, let us trace its subsequent fate.

The peroxy radical can isomerize by the reaction

(3) 

$$\sim \underset{H}{\overset{H}{C}} - O - \underset{H}{\overset{\overset{O^\bullet}{O}}{C}} - O - \underset{H}{\overset{H}{C}} \sim\rightarrow 2 \sim \underset{H}{\overset{H}{C}} - O - \underset{H}{C} = O + OH^\bullet, \qquad (3)$$

proceeding monomolecularly with an activation energy of ~ 20 kcal/mole (^{7}). $W_3 = 2.5 \cdot 10^3[RO_2]$, or it can form a peroxide by the reaction

(3’) 

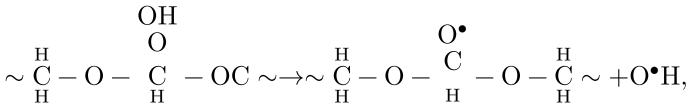
$$\sim \underset{H}{\overset{H}{C}} - O - \underset{H}{\overset{\overset{O^\bullet}{O}}{C}} - O - \underset{H}{\overset{H}{C}} \sim + HR \rightarrow \sim \underset{H}{\overset{H}{C}} - O - \underset{H}{\overset{\overset{OH}{O}}{C}} - O - \underset{H}{\overset{H}{C}} \sim + R^\bullet. \qquad (3')$$

The preexponential factor of process (3′) for many hydrocarbons is 10^{-16}–10^{-17}, while the activation energy varies from 5 to 14.5 kcal/mole (^{8}).

Taking the mean value of the activation energy as 7 kcal/mole, the reaction rate is
$W_{3'} = 4 \cdot 10^{-20}[RO_2][RH]$.

The concentration of C–H bonds in the polymer melt is $3 \cdot 10^{22}$ molecules/cm^3; then the ratio of the rates of reactions (3) and (3′) will be $W_3/W_{3'} = 2$. Thus, the peroxy radical isomerizes or gives peroxide with equal probability.

Let us estimate the possible concentration of peroxide in our system, if its decomposition occurs only by the reaction of monomolecular decomposition



$$\sim \underset{H}{\overset{H}{C}} - O - \underset{H}{\overset{\overset{OH}{O}}{C}} - OC \sim\rightarrow \sim \underset{H}{\overset{H}{C}} - O - \underset{H}{\overset{O^\bullet}{C}} - O - \underset{H}{\overset{H}{C}} \sim + O^\bullet H,$$

proceeding with activation energy $E = 30$ kcal/mole (^{9}),

$$W = 4 \cdot 10^{-2}[\mathrm{RCOOH}].$$

The change in the peroxide concentration is

$$\frac{d[\mathrm{RCOOH}]}{dt} = W_{\mathrm{form}} - W_{\mathrm{decomp}} = 2.5 \cdot 10^{3}[\mathrm{RO_2}] - 4 \cdot 10^{-2}[\mathrm{RCOOH}].$$

The concentration of radicals $[\mathrm{RO_2}]$ can be found from the equation:

$$\frac{d[\mathrm{RO_2}]}{dt} = (K_{1'} + K_{2'})[\mathrm{R}][\mathrm{O_2}] - K_3[\mathrm{RO_2}] - K_{3'}[\mathrm{RO_2}][\mathrm{RH}].$$

In the presence of long chains, the rate of the oxygen-addition reaction must be equal to the sum of the rates of hydroperoxide formation and isomerization, i.e.,

$$[K_{1'} + K_{2'}][\mathrm{R}][\mathrm{O_2}] = K_3[\mathrm{RO_2}] + K_{3'}[\mathrm{RO_2}][\mathrm{RH}].$$

We estimated the values of all constants above; therefore it is easy to find the relation between the concentrations [R] and $[\mathrm{RO_2}]$

$$[\mathrm{RO_2}] = 0.6[\mathrm{R}].$$

The experimentally determined maximum gas-evolution rate, equal to $2.5 \cdot 10^{19}$ molecules/sec • cm^3, is nothing other than the rate of reaction (2).

Hence, $[\mathrm{R}] = 2.5 \cdot 10^{14}$ molecules/cm^3. Therefore, $[\mathrm{RO_2}] = 1.5 \cdot 10^{14}$ molecules/cm^3. Then

$$\frac{d[\mathrm{RCOOH}]}{dt} = 4 \cdot 10^{17} - 4 \cdot 10^{-2}[\mathrm{RCOOH}]; \qquad [\mathrm{RCOOH}] = 4 \cdot 10^{17}(1 - e^{-0.04t}).$$

It follows from the calculation that the maximum possible concentration of peroxide is $4 \cdot 10^{17}$ molecules/cm^3. Such a value is analytically determi-

Since the presence of peroxides was not detected experimentally, it may be expected that they either are not formed at all or are consumed in an additional reaction not taken into account by us.

In conclusion, we note that none of the reactions considered above leads to the formation of formic acid, which is found among the degradation products of PFA in considerable amounts (5–8%). The study of the pathways and sources of HCOOH formation during the oxidative degradation of PFA should be the subject of a separate investigation.

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Note: Figure translations are in progress. See original paper for figures.

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