

Thermal Decomposition of Polytetrafluoroethylene in Various Gaseous Atmospheres^{1,2}

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The effects of various gaseous atmospheres on the thermal decomposition of polytetrafluoroethylene have been investigated in the range 450° to 500° C. Both catalysis and inhibition were observed. The inhibitory substances, chlorine, hydrogen, carbon tetrachloride, and toluene, all produced marked changes in the mechanism of polytetrafluoroethylene decomposition. Whereas the normal degradation reaction in a vacuum produces mainly monomer, the inhibited reactions give large fragments plus side reactions, such as the defluorination of the skeletal carbon structure. The results can be interpreted in terms of previous theoretical treatments of chain mechanisms for polymer decomposition and lead to the conclusion that, although the inhibited reactions produce little monomer and are highly random, the relatively high rates observed indicate induced decomposition by the inhibitory substances. Energetic considerations are discussed and appear consistent with the postulated mechanisms.

1. Introduction

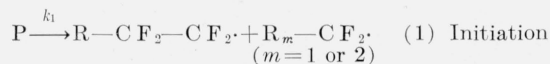
The thermal decomposition of polytetrafluoroethylene in vacuum has been studied in some detail by Madorsky and coworkers [1]³. Although Madorsky et al. report that the polymer degrades by a first-order rate law, close inspection of their data (fig. 1) reveals that this is only strictly true at temperatures above about 510° C, whereas below about 480° C the polymer degrades by a zero-order law.

The existence of the zero-order law governing the kinetics of degradation at temperatures lower than about 480° C has been confirmed by one of the present experiments, the data of which are plotted in figure 2. Here, the weight-loss-versus-time curve for the degradation performed in a flow system under nitrogen is given. The plot shows that after an initial slight dip the rate is constant up to about 40 percent of volatilization at 460° C. In the temperature range studied, however, the energy of activation obtained from extrapolated initial rates was 80 kcal, as reported by Madorsky [1].

During the degradation the polymer retains its rigid form to about 50-percent conversion, after which it softens. During this pyrolysis, close to 100 percent of the volatile matter is monomer.

Most polymer decompositions can be treated in terms of a mechanism analogous to polymerization involving four elementary processes: initiation, propagation, transfer, and termination [2]. In the case of this polymer, however, the characteristics of the rate versus conversion curves (fig. 1) and the type of products obtained from the decomposition lead one to the conclusion that a chain mechanism is operative and that little transfer is occurring.

Therefore, only three of these reactions have been considered here:



The P represents any size polymer, R is part of a polymer chain, and the *k*'s are the specific rate constants.

The mechanism then is one in which a bond breaks, probably at the ends, forming radicals that unravel into monomer and eventually terminate by one or more of the processes listed.

The amount of unraveling per initiation or termination act is the kinetic chain length, γ , and a variation in this can influence the order of the rate with respect to mass, as shown in figure 3. Here are plotted theoretical curves, the upper two showing the over-all rate for this type of process, in which a polymer had an initial degree of polymerization of about 1,000 and a kinetic chain length of 10^4 and 10^3 , respectively, with a given rate of initiation. With the same rate of initiation but now restricted to end initiation, and with little or no unraveling, i. e., $\gamma=1$, the dashed curve would apply, which has about 0.001 the initial rate of the upper curve. This dashed curve gives a zero-order rate with respect to mass, which would be the situation if complete inhibition could be produced.

The change in order of rate of degradation of polytetrafluoroethylene from zero to first order with increase in temperature may indicate an increase in

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³ Figures in brackets indicate the literature references at the end of this paper.

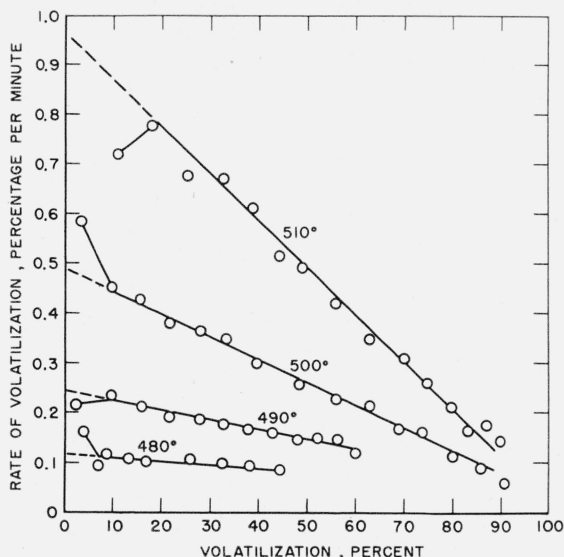


FIGURE 1. Rate of thermal degradation of polytetrafluoroethylene in a vacuum as a function of percentage of volatilization [1].

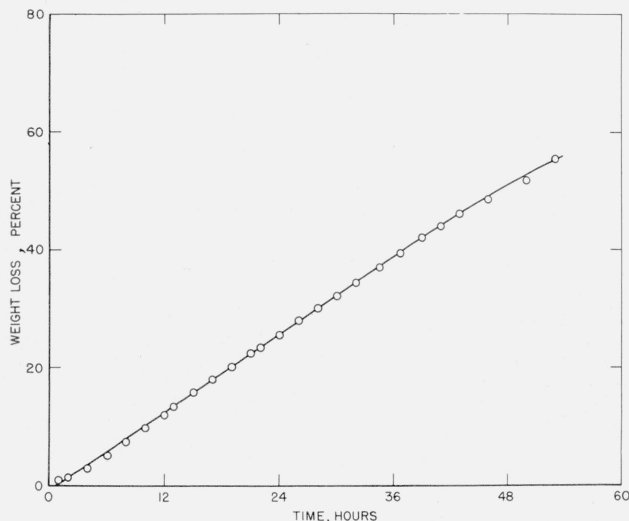


FIGURE 2. Thermal degradation of polytetrafluoroethylene in flow system under nitrogen at 460° C.

kinetic chain length from a value much lower than the degree of polymerization at temperatures of degradation below about 480° C to a value equal to or greater than the degree of polymerization at temperatures above 510° C. A possible alternate explanation could be that a surface effect is important at the lower temperature range, such that the rate is proportional to the surface area of the degrading polymer, whereas at high temperatures the rate eventually becomes proportional to the bulk of the material. However, in the experiments under gases reported here, surface effect does not appear to exist to any great extent because the surface area was varied in this study.

The curve with a maximum in figure 3 represents the behavior for a purely random degradation of a

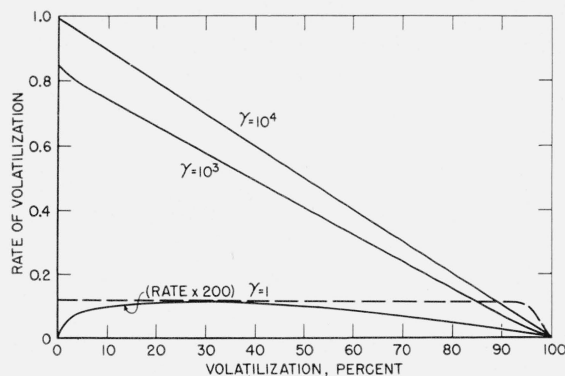


FIGURE 3. Rate of volatilization as a function of conversion and kinetic chain length with random initiation (solid line) and end initiation (dashed line) [2].

polymer. Random degradation may be the result of only random initiation, or of a high number of transfer reactions, if in either case a small number of depropagation or unraveling acts occur. A much slower over-all rate should result if the random effect is due to the initiation step alone.

Whenever a reaction proceeds by a chain mechanism it should be possible, in theory, to inhibit the over-all reaction by adding a reagent that would in effect make reaction 4 in the above mechanism more probable than is normal for the uninhibited reaction. Changing the history of the polymer in regard to catalyst and structural contaminants has previously been shown to have little effect on the rate of degradation [3]. However, in the thermal decomposition of hydrocarbons, various conditions of inhibition have been studied by Rice and Polly [4] and Hinshelwood and coworkers [5]. For gas-phase reactions inhibition has been shown to be produced by some gases, e. g., NO and CH_3CHCH_2 . In solid polymers, and especially in polytetrafluoroethylene, one of the difficulties would be poor accessibility of the inhibitor to the radical chain carrier. This difficulty was borne out by the failure to alter appreciably the course of its degradation in over 40 experiments in which solid reagents that were considered to be potential inhibitors were intimately mixed with the polymer. On the other hand, gases can diffuse much more readily throughout a reaction medium and hence offered, on a priori considerations, the best possibility of influencing the course of the reaction.

2. Experimental Reagents

The polymer used was in the form of a water suspension obtained from E. I. duPont de Nemours & Co., Inc. and designated by them as TD-3. The suspension was frozen and then dried in a vacuum, and the powder so obtained was employed in the majority of the experiments.

The gases used were the purest obtainable from the Matheson Co., Inc. The toluene was Baker & Adamson's ACS grade.

3. Procedure

The rate of degradation was measured by determining the weight loss of the polymer after periodic heating under the various flowing gases. The sample of polymer was usually about 1g and was placed in a porcelain boat for heating. The boat was heated in a horizontally placed hard-glass tube surrounded by a brass furnace that covered about one-third of the tube. The gas and boat were introduced into one end of the tube, and the gas was exhausted at the other end. The boat was inserted into the tube via a female 34/45 standard-taper glass ground joint, after which the tube was capped with a male 34/45 standard-taper ground joint. A heavy nichrome wire passing through a small tube in the cap, and sealed with a rubber stopper, enabled the operator to move the porcelain boat while in the tube in and out of the furnace.

In a typical measurement the boat containing a weighed sample of polymer was placed in the unheated portion of the tube. The system was then thoroughly flushed with the gas under study and a steady flow maintained. The temperature of the furnace was brought to the desired level. The boat was then pushed into the furnace. The manually operated variable transformer sometimes had to be readjusted in order to maintain the desired temperature. Temperature equilibrium was usually reached about 3 to 4 min after the introduction of the boat into the furnace. The time at which the temperature reattained the desired value was taken as the zero time for that particular run. At the end of a given interval of time (usually 1 hr) the boat was withdrawn from the furnace into the unheated part of the tube. This time was taken as the end of the interval of pyrolysis. Experience showed that it made no difference whether the boat was then withdrawn from the tube and allowed to cool to room temperature in the air or left in the tube to cool.

The temperature of the furnace was measured by means of an iron-constantan thermocouple read on a potentiometer. The thermocouple was centered in the furnace by means of a thermocouple well, securely attached to the cap. The temperature was determined at a position above the boat and was steady to ± 2 deg C.

When pyrolyzed in a vacuum or under nitrogen, polytetrafluoroethylene retains its original form. In the experiments reported here the polymer, with one exception, became very fluid at the temperature of pyrolysis. Although the molecular weight of the polymer cannot be determined quantitatively, this change in viscosity from a solid to a very fluid liquid was taken as an indication of a very pronounced drop in molecular weight during the course of pyrolysis under the gases. }

4. Results

The gases studied may be divided into three groups: (1) those exhibiting a strong catalytic effect on the rate of degradation, i.e., O₂, NO, H₂S, and SO₂; (2) those producing an initial inhibitory effect, i.e., H₂, Cl₂, CCl₄, and toluene; and (3) those that

show neither effect, i.e., N₂ and benzotrifluoride. The rates under nitrogen (e.g., 0.017%/min at 457° C) are quite close to those observed previously in vacuum work (0.017%/min at 453° C) [1]. Consequently, results under nitrogen are used for comparison purposes.

TABLE 1. Gaseous products from the decomposition of polytetrafluoroethylene under various gases

Product	Gaseous atmosphere			
	O ₂	H ₂	Toluene	Cl ₂
Perfluoroethylene.....	Mole %	Mole %	Mole %	Mole %
Silicon tetrafluoride.....	19	33	45	(a)
Carbon dioxide.....	63	33	9	(a)
Carbon monoxide.....	18	-----	23	(a)
Trifluoromethane.....	-----	-----	18	(a)
Perfluorocyclobutane.....	-----	-----	5	(a)

^a Not identified. The products, besides an excess of chlorine atoms, showed ions in the mass spectrograph containing several chlorine atoms as well as oxygen and silicon. For example, the following ions were tentatively identified: CCl₃, SiCl₃, SiCl₂F₂, OSiCCl₃, and SiC₂Cl₄. The largest of these peaks, mass 161, was 11.7 percent of the maximum peak (mass 70, that is, Cl₂³⁵).

4.1. Catalytic Effect

The curves representing the degradation of polytetrafluoroethylene at 457° C under the various gases exhibiting a catalytic effect are shown in figure 4.

In the degradation under oxygen the polymer remained white and solid throughout the entire conversion. This fact, plus the catalytic effect and the absence of monomer in the products lead to the belief that the gas attacks the free radicals and increases, in effect, the rate of propagation. The analyses obtained from the mass spectra of the gases evolved from this experiment are listed in table 1.

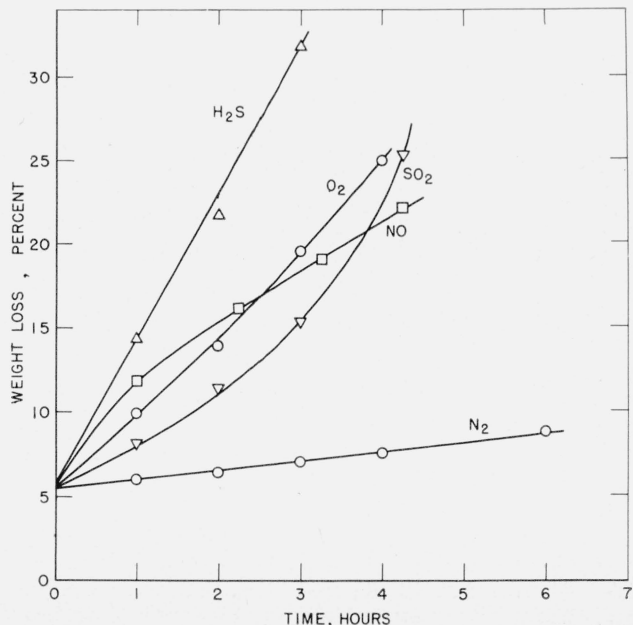
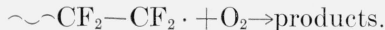


FIGURE 4. Weight loss of polytetrafluoroethylene at 457° C. under various gases having a catalytic effect on the thermal degradation.

The lack of monomer and the presence of SiF_4 and CO_2 are noted. A very small quantity ($<1\%$) of other silicon derivatives were also observed but were not identified. These results appear to indicate a reaction of the type:



The primary products may consist of labile compounds, possibly CF_2O , that quickly decompose on the glass at the temperature of pyrolysis to give the observed compounds. There appears to be no attack on the polymer because this would be expected to result in a darkening of the polymer and/or a drop in molecular weight to give a residue of high fluidity at the temperature of pyrolysis.

When present at high concentrations in the thermal decomposition of hydrocarbons, nitric oxide has been shown [5] to catalyze the rate of decomposition. At the high concentrations used here, the nitric oxide also seems to have an over-all catalytic effect. The polymer darkened slightly initially, and as conversion increased, the residue became clear and very fluid. This, plus the fact that the rate starts to level off, would seem to indicate that not only an induced initiation by some transfer mechanism is taking place, but also some product is being formed that stabilizes the degrading free radicals or polymer.

In the experiment with hydrogen sulfide the polymer quickly blackened and became fluid at its temperature of pyrolysis. During the course of this experiment the apparatus became coated with sulfur.

As the apparatus was etched from other experiments, it was not known definitely whether or not hydrogen fluoride was produced here; it presumably was. These results would seem to indicate induced initiation and defluorination.

With sulfur dioxide the polymer became black and gelatinous. Again, this is indicative of induced decomposition and defluorination with no inhibition. The increasing rate of degradation as shown in figure 4 supports this.

4.2. Inhibition Effects

In figures 5, 6, and 7 are plotted the weight-loss-versus-time data for the thermal decomposition of polytetrafluoroethylene under hydrogen, chlorine, and toluene. Carbon tetrachloride also showed good inhibition initially, but as at later stages, the inhibition was much less effective than with the above three compounds, the system was not studied in detail.

It will be immediately noted on comparing these results with those obtained for the pyrolysis of polytetrafluoroethylene under nitrogen, figure 2, that the characteristics of the reaction have completely changed in that all the curves for the gas studies have a definite inflection point. Consequently, when the rate is plotted against conversion, figures 8, 9, and 10, it is seen that all the graphs have definite maxima and that initially the rates are much lower than those for the vacuum work, figure 1. These curves are typical of those obtained for mechanisms with large random components [2]. Random initiation or very

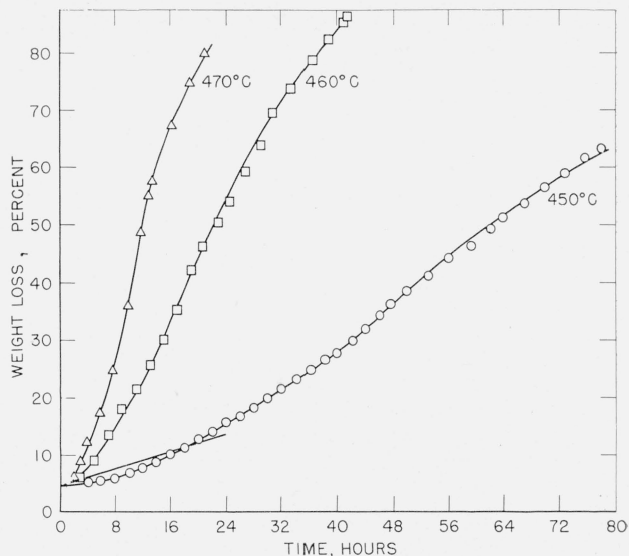


FIGURE 5. Weight loss of polytetrafluoroethylene under hydrogen at several temperatures.

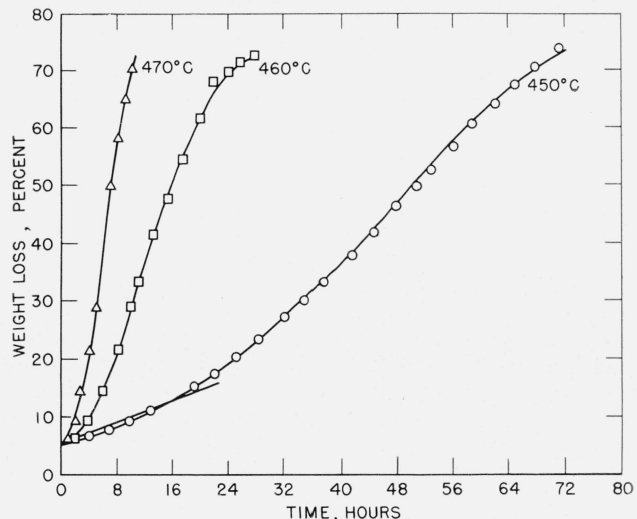


FIGURE 6. Weight loss of polytetrafluoroethylene under chlorine at several temperatures.

frequent transfer with short propagation and termination usually give rise to such results. It has been recently demonstrated that the thermal decomposition of polymethylene follows such a pattern [6]. This type of mechanism leads to a very fast drop in molecular weight, and this has been noted in these experiments, because the polymer quickly became very fluid.

The experiments with chlorine as the inhibitor did not show any consistent color change in the polymer. Also, an analysis of the polymer after 80-percent degradation showed a chlorine content of 0.6 percent by a microcombustion method. All this is compatible with the idea that the mechanism of the observed inhibition involves the combination of polymer radicals with the chlorine atoms produced. An analysis

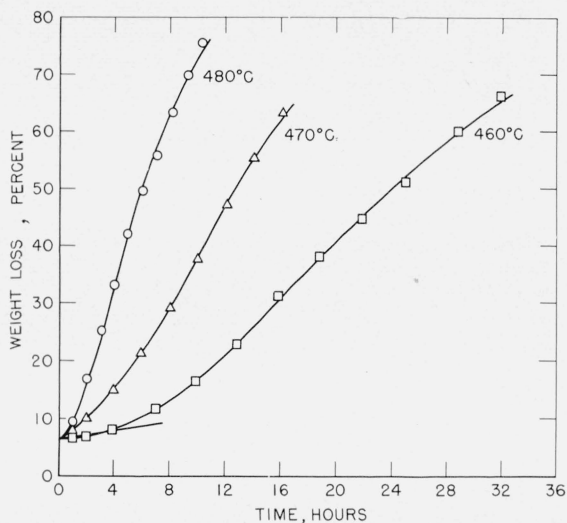


FIGURE 7. Weight loss of polytetrafluoroethylene under toluene diluted with nitrogen at several temperatures.

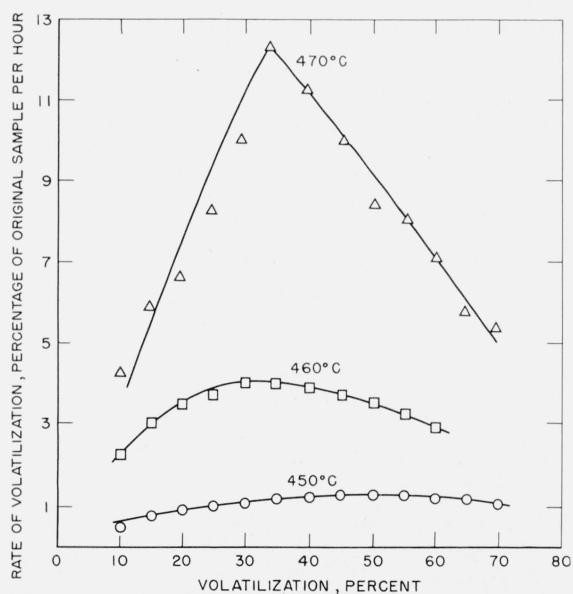


FIGURE 8. Rate of volatilization of polytetrafluoroethylene under hydrogen as a function of conversion at several temperatures.

of the gaseous products, table 1, is very complicated, consisting mostly of silicon, halogen, and carbon-containing compounds. These again would seem to result from the decomposition of labile primary products on the glass.

In the experiments with hydrogen there is, besides the molecular weight drop, a blackening of the polymer. At very high conversions (about 65%) the residue becomes hard. Concurrent with all this is an etching of the glass tube. An analysis of the gaseous products, table 1, shows that some monomer is produced, as well as carbon dioxide and silicon tetrafluoride. These results again indicate random degradation, but with the added feature of defluorination by hydrogen.

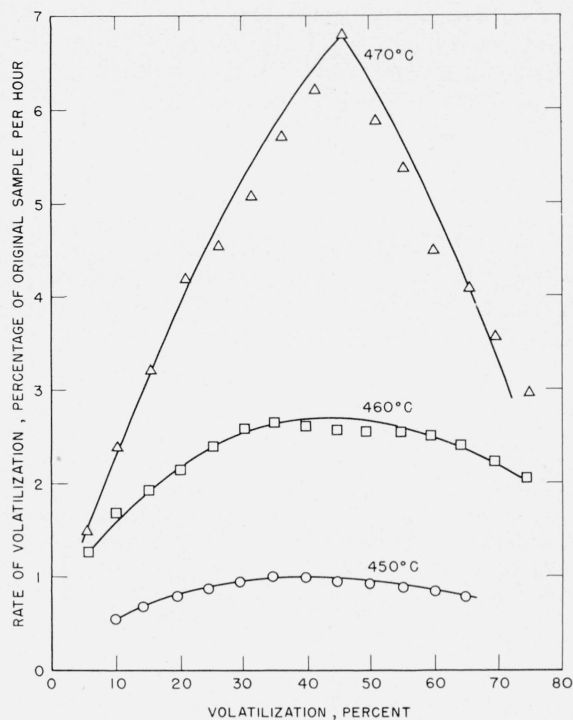


FIGURE 9. Rate of volatilization of polytetrafluoroethylene under chlorine as a function of conversion at several temperatures.

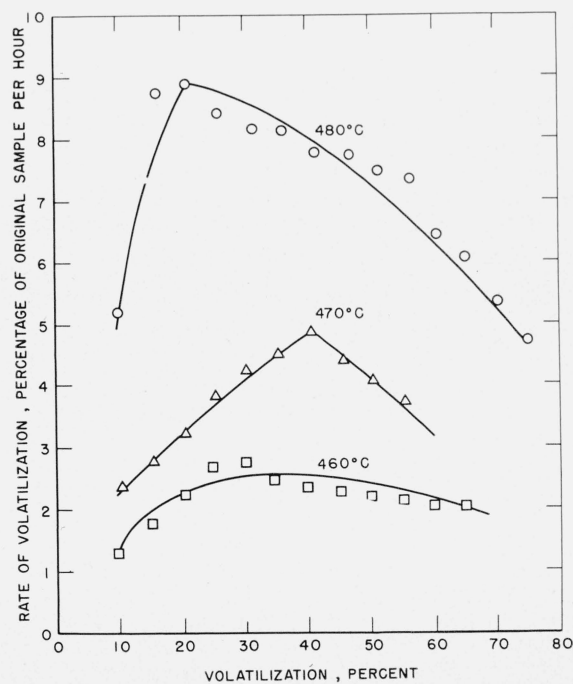


FIGURE 10. Rate of volatilization of polytetrafluoroethylene under toluene diluted with nitrogen as a function of conversion at several temperatures.

The experiments with toluene give results similar to those with hydrogen. However, defluorination is much more prevalent and may actually be rate determining, because the residue, after becoming liquid, soon hardens to a brittle mass at about 30-percent conversion. The analysis of gaseous products is given in table 1. Here again there is some monomer formed, as well as silicon tetrafluoride and carbon dioxide. The somewhat larger amount of monomer may mean relatively less effective reaction of the vapor with decomposing polymer free radicals.

5. Discussion

In any kinetic discussion some idea of the various bond strengths is valuable. However, the carbon-carbon-bond strength in fluorocarbons is in doubt. A value of 124 kcal for the carbon-carbon bond in hexafluoroethane has been reported by Dibeler, Reese, and Mohler [7] as obtained in electron-impact experiments. However, a recent, separate determination of the ionization potential of the per-fluoromethyl radical by Lossing [8], using the electron-impact method, has lowered this value for hexafluoroethane to 95 kcal.

An analysis of the best thermochemical data on the subject would seem to favor a value about half way between these two extremes. Using the high and rather generally accepted value of the heat of sublimation of graphite, i. e., $L(C) = 170.6$ kcal, together with the heat of formation of carbon tetrafluoride, 220 kcal [9, 10], an average carbon-fluorine bond of 116 kcal is obtained for this compound. Now in hydrocarbons the average carbon-hydrogen bond strength in ethane is about 8 percent less than those in methane. If in fluorocarbons the carbon-fluorine bond strengths drop off by approximately the same percentage in going from carbon tetrafluoride to hexafluoroethane, then the average carbon-fluorine bond strength in hexafluoroethane should be about 107 kcal. This, taken with the heat of formation of hexafluoroethane of 303 kcal, as obtained by Duus [9], gives a carbon-carbon bond strength for this fluorocarbon in the neighborhood of 112 kcal.

If the interpretation of the kinetic data along the lines of the existing theories is correct and polytetrafluoroethylene does decompose by end initiation with the average carbon-carbon bond strength being close to that in hexafluoroethane, e. g., 110 kcal, it should be possible to deduce the strength of the bond broken in the end initiation (see section 1), i. e., E_1 . Taking the only value available for the molecular weight of polytetrafluoroethylene, i. e., 200,000 [11], and realizing that for end initiation to have a predominant effect on the kinetics, this rate of initiation must be 10 times faster at about 500° C than that for random initiation, it is found that there must be a difference of at least 15 kcal between the strength of the weak end bond and that of the average bond. This gives the value of 95 kcal, which was used for end initiation.

In the experiments described it appears that the various gases have in some cases altered the

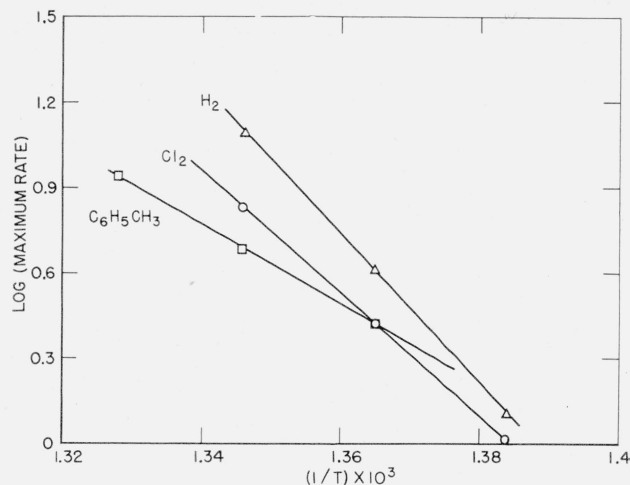


FIGURE 11. Activation energy slopes for the thermal degradation of polytetrafluoroethylene under hydrogen, chlorine, and toluene.

mechanism of the degradation of polytetrafluoroethylene. The gases that act as inhibitors have introduced a random quality to the over-all degradation.

In this random type of degradation as ascertained from the kinetic curves (fig. 8, 9, and 10), the maximum rates are the most dependable and the most significant from which to calculate energies of activation. The maximum rate of volatilization has been related [2] to the specific rate constant for a purely random reaction as follows:

$$[dC/dt]_{\max} = k \frac{L}{e}$$

where C is conversion, t is time, k is a composite specific rate constant for the over-all reaction, e is the base of the natural logarithm, and L is the critical chain length for vaporization (i. e., the size for which rate of decomposition equals rate of vaporization) and is here assumed to be a constant. In terms of elementary chain mechanism and the total radical concentration R ,

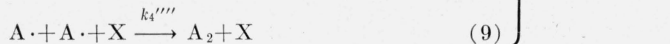
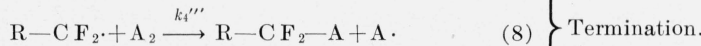
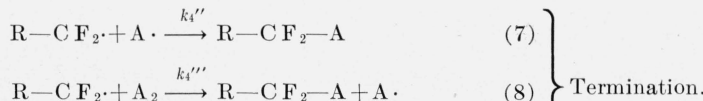
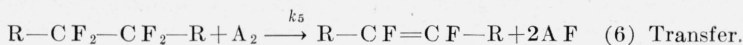
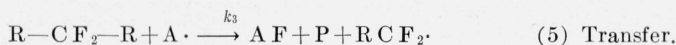
$$k = k_1 + k_3 R = k_3 (I/k_4)^{1/2} \quad (\text{when } k_1 \text{ is small}),$$

where I is the rate of initiation of active centers, k_3 the rate constant for transfer, and k_4 the rate constant for termination.

Taking the maximum rate from the experimental curves as proportional to the specific rate constant and making Arrhenius-type plots of the data, straight lines are obtained, as shown in figure 11.

From the slopes of these lines energies of activation are obtained. In the case in which chlorine was the inhibiting gas, a value of 100 ± 4 kcal is obtained. With hydrogen, a value of 118 ± 4 kcal is obtained, and toluene gives 64 ± 5 kcal.

The experimental results and theory can apparently be brought together if a mechanism of the following type is assumed, where, beside the three elementary reactions mentioned above, there is



} Termination.

Here A_2 is the inhibiting gas, P and $R-CF_2 \cdot$ are the polymer and polymer radicals, respectively, and X is the third body required for this reaction.

In the experiments with chlorine the low bond energy of this molecule should favor the formation of these atoms as the potential chain carriers. As the concentration of these atoms would be relatively high, the possibility of a chain transfer by reaction 5 and a molecular-weight drop would be increased, having an over-all effect of inducing the polymer decomposition. The lack of monomer in the gases evolved would seem to indicate that reaction 2 is suppressed, presumably owing to the termination of the polymer radicals by reactions 7 or 8, resulting in inhibition. The over-all chain termination would, then, seem to be by reaction 9, because the chlorine atoms would constitute the largest source of chain carriers. As the polymer is colorless throughout the degradation, reaction 6 would not likely be operative, as that would be expected to cause darkening of the polymer.

With this mechanism the over-all energy of activation would be expected to be related to those of the elementary steps as follows:

$$E = \frac{1}{2}E_1' + E_3 - \frac{1}{2}E_4'''$$

$$100 = \frac{57}{2} + E_3 - 0$$

$$E_3 = 71.5 \text{ kcal.}$$

Here 57 kcal is the dissociation energy of the chlorine molecule [12]. This rather high value for E_3 would seem to be the energy necessary for a chlorine atom to abstract a fluorine atom from the polymer, which reaction must be assumed in order to explain the high maximum rate and the molecular-weight drop.

When hydrogen is the inhibitor, the situation is slightly different. It is thought that the chain initiation step is the breaking off of a volatile fragment from the ends of the polymer, as shown by reaction 1, followed by unzipping of the polymer radical to give some monomer, reaction 2 (see table 1), but finally terminating by reaction 8. This mode of initiation of the reaction is assumed in place of hydrogen dissociation because the bond strength of hydrogen is higher than the 95 kcal of

this reaction. Chain unzipping would be inhibited by reaction 8, and the hydrogen atom so formed probably induces further decomposition in the polymer by reaction 5. A side reaction such as reaction 6 would account for the darkening of the polymer but, due to the small mass of material vaporizing in this way, would probably not drastically affect the over-all rate. Final termination of the over-all chain reaction would seem to be most likely by reaction 7 if a steady state is truly obtained.

In this inhibition under hydrogen, the over-all energy of activation for this random process is broken down as follows:

$$E = \frac{1}{2}E_1 + E_3 - \frac{1}{2}E_4''$$

$$118 = \frac{95}{2} + E_3 - 0$$

$$E_3 = 70.5 \text{ kcal.}$$

These values obtained for the energy of activation for transfer, i. e., E_3 , are high and constant within the experimental error of the experiment, e. g., 71 ± 4 kcal. As this step probably comprises two steps, one the abstraction of fluorine by a radical, and the other the breaking up of the polymer radical in a depropagation step, this high and apparently constant value is probably due to the propagation step E_2 .

In the case of the toluene inhibition, an initial drop in molecular weight and the defluorination can be explained by the above reaction scheme, as in the case of hydrogen and chlorine. Here, formation of hydrogen atoms and benzyl radicals may be the most important initiation step (reaction 4), which in time should lead to chain transfer, reaction 5, and hence induced decomposition of the polymer. Termination by reactions 7 and 9, where benzyl radicals are important, would end the chain reaction. The observed inhibition could be explained by reactions 7 and 8. The presence of the defluorination by reaction 6, as evidenced by early hardening of the polymer, complicates the over-all rate. Therefore, it is not possible to identify the energy of activation obtained from the toluene experiments, i. e., 64 ± 5 kcal, as a single entity or a function of elementary energies of activation.

6. References

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