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Study of Self-Ignition of PVC

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ABSTRACT

The self-ignition of rigid PVC has been studied under static and dynamic conditions. Only a high-temperature boundary has been found, and the self-ignition temperature in air at atmospheric pressure lies between 555 and 560°C. The effect of preliminary HCl evolution has been investigated, and it is shown that the more the HCl evolution, the higher the self-ignition limit. It has been impossible to make polyacetylene ignite spontaneously in the presence of HCl in oxygen up to 900°C. This is attributed to a special role of HCl in combustion of PVC. The rate of HCl release was measured by a potentiometric method, and the overall activation energy of the process was found to be 9.4 kcal/mole. This low value seems to be due to the presence of oxygen. Chromatographic analysis showed CH_4 and CO to be the major gaseous products of oxidation of PVC in this parametric zone.

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INTRODUCTION

PVC, due to its particular structure, exhibits a poor combustibility. This renders ignifugation research on this subject almost purposeless. Nevertheless two nuisances are attached to the presence of PVC in a fire: HCl evolution and smoke formation. We shall not discuss here this second point since it is not really specific to PVC.

Hydrochloric acid can lead to catastrophic consequences when conditions are such that it induces significant degradation, even when released in small quantities (computers for example). As we shall see, PVC exhibits self-ignition only at high temperature. Considerable work has been done on dehydrochlorination between 80 and 250°C. It has been generally shown that the resulting material is a highly conjugated polyene, polyacetylene (PA). This material is very interesting, especially when considered through its self-ignition properties. In the following we shall examine the chemical behavior of PVC close to its self-ignition limit.

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EXPERIMENTAL

The phenomenon of self-ignition of PVC can suitably be observed by means of an apparatus we have devised in our laboratory [1] and the principle of which is briefly summarized in Fig. 1a. The silica reactor permits use of the apparatus up to 900°C. Nevertheless above 500°C an infrared filter is needed if one wants proper observation of the light emission from the reaction. But, most frequently this reaction was followed by its thermal effect by means of a Chromel-Alumel thermocouple (80 μm). Two different techniques have been used to determine the concentration of products as a function of time or temperature. First, HCl was titrated by a potentiometric method according to Tho and Roux [2], either by discontinuous trapping of the products from the static vessel (Fig. 1a) or by a dynamic method by use of a slightly modified apparatus as shown in Fig. 1b. In this latter case, HCl was transferred to the measuring cell within a certain delay which could be determined (in our conditions it was generally 30 sec). A double trace recorder showed simultaneously the temperature in the neighborhood of the sample and the emf of the cell as a function of time. Figure 2 represents a typical recording of such curves between which the temporal shift has been corrected. A difficulty which became apparent was interpretation of the results of titration, due to the fact that it was difficult to estimate the extent to which chlorine was present in the reaction vessel according to

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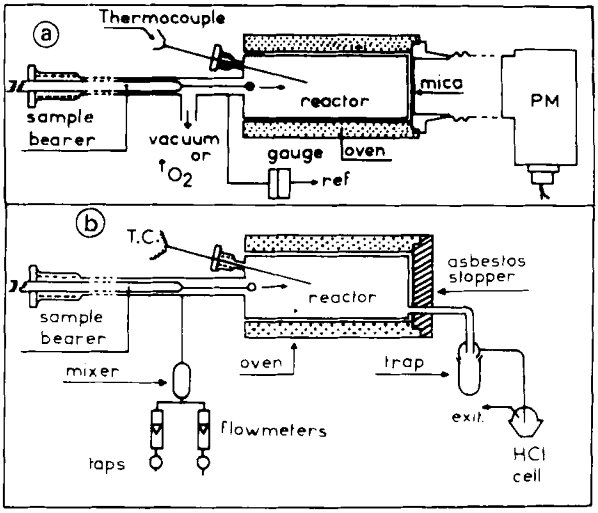

FIG. 1. Schematic diagram of the self-ignition apparatus: (a) static (b) dynamic.

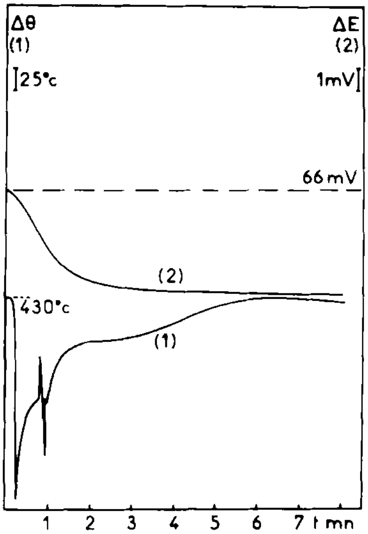

FIG. 2. Typical simultaneous recording of (1) $\Delta\theta$ and (2) emf of HCl cell. PVC = 100 mg; θ = 430°C; $[O_2]$ = 57% ($+N_2$) = P_{atm}.

Deacon equilibria. The equilibrium constant, defined as

$$K_p = P_{Cl_2}{}^2 P_{H_2O}{}^2 / P_{HCl}{}^4 P_{O_2}$$

equals 2.4 at 419°C [3]. In our particular conditions this could have led to a somewhat significant value of the chlorine concentration. Nevertheless, the K_p value becomes the smaller the higher the temperature, leading to a decrease in the chlorine concentration. Theoretically, chlorine would be troublesome at lower temperatures. Fortunately the equilibrium rate remains very low even at 400°C [3]. Nevertheless we chose a rather high value of the flow rate of oxygen above the PVC sample to prevent chlorine formation.

Second, we used gas chromatography. Lighter hydrocarbons and CH_3Cl were analyzed on a Porapak Q column (3 ft × 1/4 in.) with an FID detector, CO, on a 5 Å Molecular Sieve column with a catharometer detector.

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RESULTS AND DISCUSSION

Phenomenology of the PVC-Oxygen System

We defined the "concentration" [1] as the value of the ratio $m_p/(m_p + m_{O_2})$, where m_p is the mass of polymer introduced in the reaction vessel and m_{O_2} the mass of oxygen. Figure 3 shows the self-ignition limit of rigid PVC slightly stabilized by 0.25% octylmercaptan tin. The concentration has been chosen sufficiently low (14.3%, corresponding to about 34 mg PVC under our conditions) to keep the reactor from getting excessively dirty. As expected, PVC exhibits a single self-ignition limit at high temperature. A low-temperature mechanism (cool flames) similar to those of polypropylene or polyethylene as we showed previously [4-6], does not exist. From this boundary we can deduce that the self-ignition temperature ($\theta_{s,i}$) in air at atmospheric pressure would be around 600°C. Nevertheless, this is exaggerated. If such an experiment is done in air (Fig. 4) it can be shown that the boundary is lowered and that the self-ignition point actually lies near 555-560°C. We have already noted this promoting influence of nitrogen in the case of polypropylene [4]. This is probably a general phenomenon. It seems to us that it is related to the diffusion of radicals to the walls of the vessel (or to the polymer surface itself).

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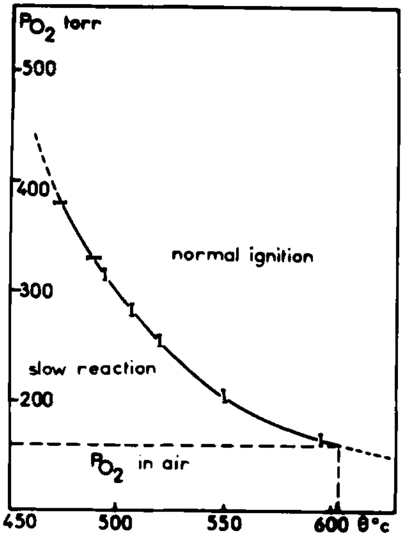

FIG. 3. Self-ignition limits of PVC as P_{O_2} vs. temperature. Isochore 14.3%; PVC + 0.25% octyl SH Sn.

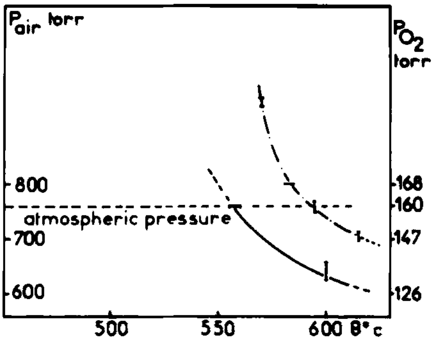

FIG. 4. Self-ignition limits of PVC as affected by N_2: (—) self-ignition limit in air; (- • -) self-ignition limit in O_2. Isochore 14.3%; PVC + 0.75% octyl SH Sn.

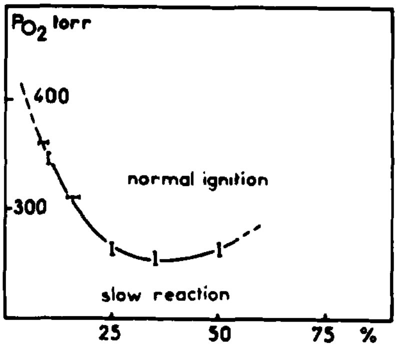

FIG. 5. Self-ignition limits of PVC as P_{O_2} vs. concentration of PVC. Isotherm 494°C; PVC + 0.25% octyl SH Sn.

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Figure 5 shows the variations of the self-ignition pressure in oxygen as a function of the concentration. It is clear that this critical pressure passes through a minimum for the value 30% of the concentration, indicating that an optimum ratio exists between the mass of polymer and the total amount of oxygen present in the reactor.

Effect of Previous Dehydrochlorination of PVC on the Morphology

The release of HCl is the phenomenon which characterizes the pyrolysis or the combustion of PVC. It is of interest to know to what extent this can modify the morphologic phenomenona. We have compared under the same conditions various samples of PVC which had been previously exposed to partial dehydrochlorination under vacuum and at temperatures not high enough to ensure further pyrolysis of the polymer, that is to say, breaking of C–C or C–H bonds, ($T < 300°C$). The quantity of removed HCl was determined by weighing the sample (a few grams) before and after each operation. The obtained product was then brought to the self-ignition device and $\theta_{s,i}$ determined as a function of oxygen pressure.

Figure 6 shows results obtained in three different cases for which the HCl loss was respectively 7, 48, and 95% of the total acid theoretically available from the sample. It is clear that the boundary is sharply raised, at least at higher values of oxygen pressure. We think that this resistance to self-ignition is the consequence of a strong

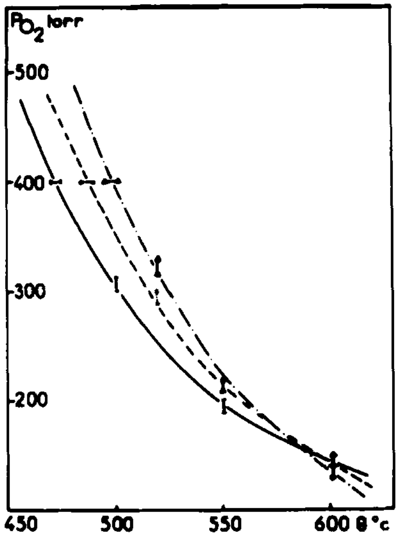

FIG. 6. Self-ignition limits of PVC as affected by previous dehydrochlorination: (—) dehydrochlorination under vacuum for 10 min at 200° C, -7% or 0 HCl; (--) dehydrochlorination for 10 min at 250° C, -48% HCl; (- • -) dehydrochlorination for 10 min at 300° C, -95% HCl. PVC + 0.25% octyl SH Sn.

resonance in the residual macromolecule, which leads to the stabilization of radicals which propagate the chains of oxidation. Within the self-ignition area, the value of the self-ignition delay ($\tau_{s,i}$) is about 30 sec. At this time almost all the available HCl has been released in the reaction vessel.

The question arises whether the ignition of PVC in pure oxygen is equivalent, as regards the mechanism of the process, to the ignition of polyacetylene in premixed O_2 + HCl gas. To elucidate this point, we devised an experiment in which polyacetylene was introduced into the reaction vessel containing HCl + O_2. The HCl concentration was calculated to equal that concentration we could have obtained from a corresponding PVC sample. In this case, we could never reach $\theta_{s,i}$ in our apparatus, the maximum working temperature of which is 900° C. It is therefore obvious that PVC self-ignition is by no way equivalent to the ignition of polyacetylene in the presence of HCl. This gas seems only to have some influence during the process of release and not by

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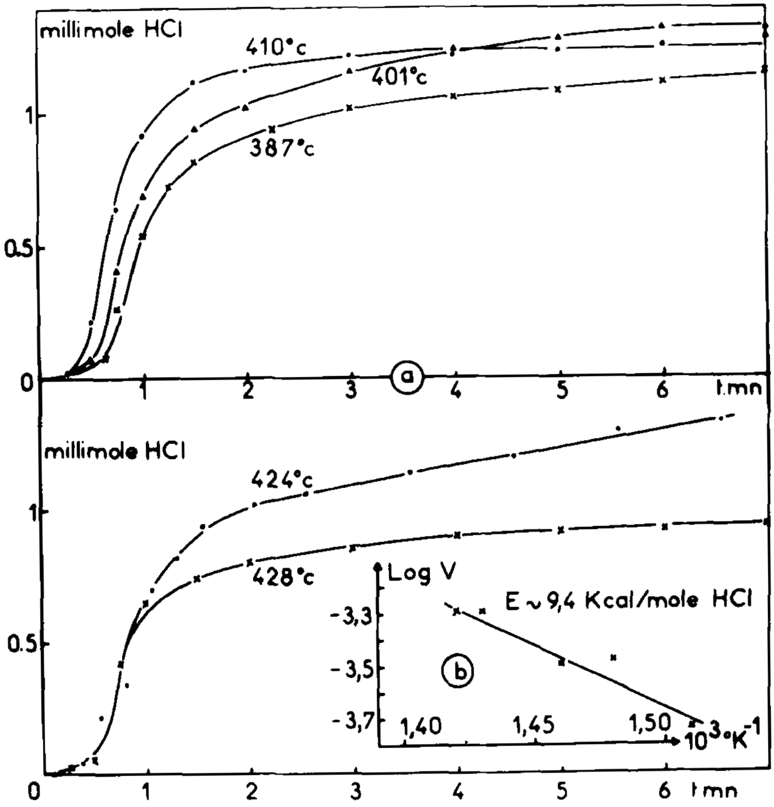

FIG. 7. Accumulation of HCl in the cell: (a) HCl vs. time at various temperatures, and (b) Arrhenius plot (inset). [O_2] = 57% (+ N_2) = P_{atm}; flow rate = 35 liter/hr; m_{PVC} = 100 mg.

its mere presence around the sample. The catalytic effect of HCl on PVC degradation has been often pointed out in the literature [7, 8]. Owing to these experiments, it seems that this catalytic effect exists also during combustion processes, but it disappears when HCl is added to oxygen.

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Accumulation of HCl and Other Products in the Vicinity of the Self-Ignition Boundary

HCl Formation

We shall discuss here only the results we obtained with the apparatus shown in Fig. 1b (dynamic). Figure 7a shows various accumulation curves of HCl at different temperatures in a flow of N_2 plus O_2 (a mixture containing 52% O_2). This concentration of oxygen had been calculated from the self-ignition boundary determination to give a significant rate of reaction. The measurements were done at atmospheric pressure with 100 mg of polymer. Returning to Fig. 2, one can see on the thermal recording a sharp perturbation. We attribute this to an explosive evolution of HCl, which is an exothermic reaction [9]. Our potentiometric method cannot follow such a fast reaction, and the emf of the cell varies then quite smoothly against time. The

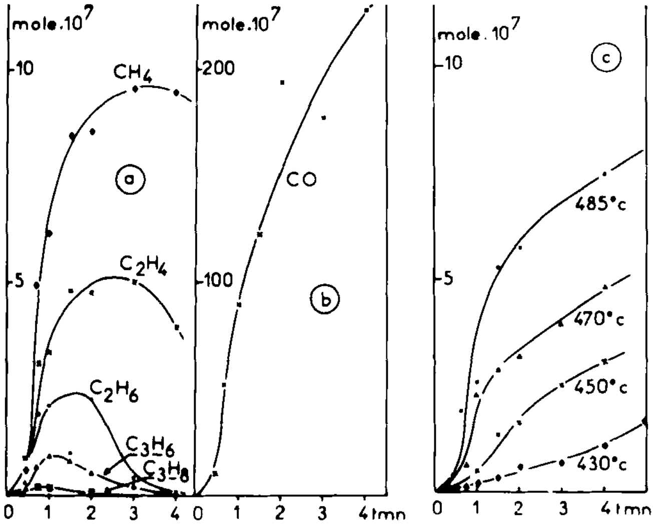

FIG. 8. Accumulation of gaseous products in a 100 ml silica reaction vessel (a) lighter hydrocarbons at 485°C under P_{O_2} = 300 Torr with 34.6 mg PVC; (b) CO at 485°C under P_{O_2} = 300 Torr with 34.6 mg PVC; (c) CH_3Cl at various temperatures under 300 Torr oxygen with 34.6 mg PVC.

curves we obtained are sigmoidal. This is in good agreement with a chain mechanism, as reported previously [9].

The maximum amount of HCl tends to diminish as the temperature is increased. It passes through a maximum between 410 and 420°C. The lack of HCl above this temperature cannot be explained by the traces of CH_3Cl we have found (see Fig. 8c), though they tend to increase with increasing temperature. The origin of this could be the retention of HCl by the polyacetylene structure, but we did not verify this.

Figure 7b shows the Arrhenius diagram from which we deduced the overall activation energy for the maximum rate of HCl release. We found a rather low value (9.4 kcal/mole) as compared to that reported by others [10] under different conditions, Guyot and Bert were concerned with pyrolysis in the absence of oxygen. Our low value points out the sharp acceleration of the process due to the oxygen.

Lighter Oxidation Products

Figure 8 shows the accumulation curves of higher products. They are in good agreement with the previous results of Le Moan and M. Chaigneau [11], who found very low traces of CH_3Cl. We did not analyze the heavier fractions of our products, since we were mostly concerned with chlorinated products, and since these same authors had reported the total absence of such derivatives at 400°C [12]. From our curves it appears that CO is the major product of oxidation, followed by CH_4. It seems reasonable to say that self-ignition of PVC occurs mostly through further oxidation of these two species.

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CONCLUSION

PVC self-ignition occurs only at high temperatures (above 400°C). It is mostly characterized by evolution of HCl at the very beginning of the process, and the self-ignition boundary is higher, the greater the previous HCl evolution. Nevertheless it appears that self-ignition of polyacetylene in a premixed HCl plus O_2 gas mixture is not equivalent to PVC self-ignition. To be active, HCl must be released during the reaction itself. The activation energy of the HCl formation in such conditions is very low (9.4 kcal/mole) and is suggestive of an accelerating effect of oxygen. Gas chromatography allowed us to identify the major gaseous products of the oxidative pyrolysis of PVC as CO and CH_4. These two species, on further oxidation are believed to be involved in further ignition of the sample at slightly higher temperatures.

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