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THERMOANALYTICAL STUDIES OF REACTIONS IN SOLID MIXTURES OF PENTAERYTHRITOL AND OXIDIZING AGENTS. I. POTASSIUM DICHROMATE * AND POTASSIUM PERMANGANATE **

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ABSTRACT

DSC and TG, supported by IR spectrophotometry and gas chromatography, were applied to the study of reactions in solid mixtures of pentaerythritol (PE), 2,2-bis-(hydroxymethyl)-1,3-propanediol, and the oxidizing agents potassium dichromate and potassium permanganate The results indicate that esterification followed by decarbonylation occurred when the mole ratio of oxidizing agent to PE was equal to or greater than 5 · 1. At lower mole ratios evidence for esterification followed by the formation of cyclic acetal intermediates was obtained

INTRODUCTION

The application of differential scanning calorimetry (DSC) and thermogravimetry (TG) to the study of mechanisms of reactions in mixtures of solids at low temperatures (20—500°C) has not been extensive. Some studies in this area include such inorganic mixtures as silver salts and potassium chloride [1], copper salts and potassium chloride [2], and groups VB and VIB metal oxides and alkali metal carbonates [3], as well as sucrose and copper sulfate pentahydrate [4], an organic application. This investigation involved the reaction between pentaerythritol (PE), 2,2-bis(hydroxymethyl)-1,3-propanediol, and both potassium dichromate and potassium permanganate. In that PE undergoes a phase change from tetragonal to what is described as "plastic" cubic at 197°C [5], much of the information was not derived from a mixture of solids as that term is conventionally understood. It is felt that this fact makes the results, at worst, no less interesting and, perhaps, even more so.

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EXPERIMENTAL

The compounds used were Baker analyzed pentaerythritol and reagent grade potassium dichromate and potassium permanganate. The oxidizing agents were ground to a fine powder and intimately mixed with the PE immediately before each curve was obtained. In this work the mixtures are identified in terms of mole ratio, where the latter is expressed as the number of moles of PE to the number of moles of oxidizing agent.

The DSC and TG curves were obtained using a DuPont 900 Differental Scanning Calorimeter and 950 Thermogravimetric Analyzer with aluminum and platinum sample pans, respectively. All samples were open to the dynamic nitrogen or air atmosphere. The heating rate was 10°C/min unless otherwise specified.

For infrared spectra samples were taken from the DSC at temperatures of interest and pressed in KBr disks. A Perkin—Elmer 137 Sodium Chloride Spectrophotometer was used.

Gas chromatograms were obtained using a Chromalytics MP-3 Thermoanalyzer and a 6 ft Poropak Q column. The mixtures were pyrolyzed at a heating rate of 12°C min^{-1} and the gases evolved were collected in a liquid nitrogen trap. Subsequently, the latter were chromatographed using a helium flow rate of 20 ml min^{-1}, a programmed temperature increase of 15°C min^{-1} from 50°C, and a thermal conductivity detector. Although the detector was operated at its lowest sensitivity, the peaks were much more intense than is usually desirable. On-scale peaks could have been gotten but to do so would have required the study of very small samples, under which circumstances it was felt that inhomogeneity might generate misleading information.

RESULTS AND DISCUSSION

Pentaerythritol

The DSC and TG curves for PE are illustrated in Fig. 1. The endothermic peak at 197°C corresponds to the PE phase change cited earlier. The endothermic weight loss which followed the phase change can be attributed to the decomposition of PE, possibly accompanied by sublimation. Figure 2 shows chromatograms obtained from gases evolved by pure PE as well as by two mixtures of PE and $K_2Cr_2O_7$ up to 250°C. Peaks 1 and 3 have been identified as due to CO_2 and H_2O, respectively. Peaks 2, 4, and 5 have not been identified. The weight loss was nearly complete by 262°C, the melting point of PE.

Pentaerythritol and potassium dichromate

The DSC and TG curves of mixtures of PE and $K_2Cr_2O_7$ are given in Figs. 3 and 4. At temperatures up to 210°C the curves for a given mole ratio are essentially the same in air as in nitrogen. Between 210 and 397°C, the melting point of $K_2Cr_2O_7$ and, hence, the temperature at which the sample is

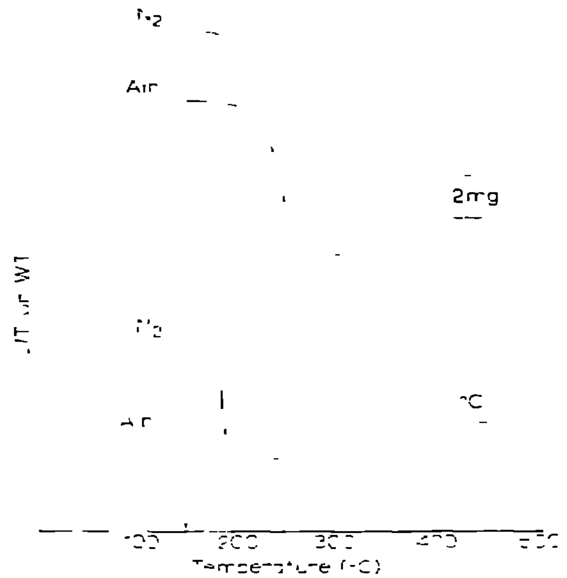


Fig. 1. DSC and TG curves of pentaerythritol.

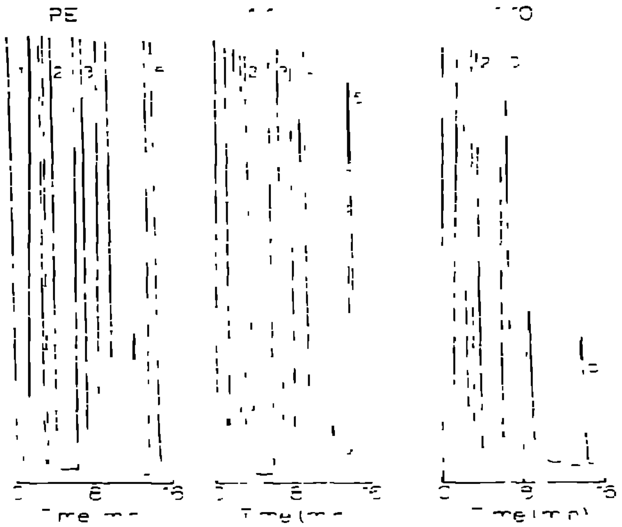
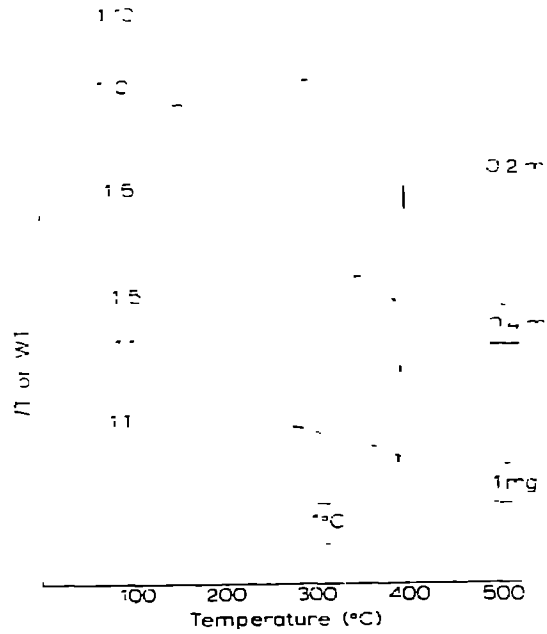


Fig. 2. Gas chromatograms of pentaerythritol and pentaerythritol—$K_2Cr_2O_7$ mixtures.



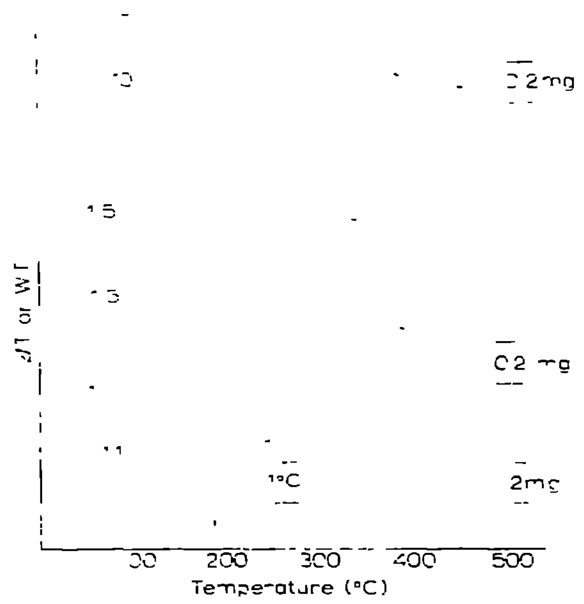


Fig 3. DSC (———) and TG (- - - - - -) curves of pentaerythritol—$K_2Cr_2O_7$ mixtures in nitrogen. 1 : 10 DSC: 2.24 mg PE, 48.5 mg $K_2Cr_2O_7$, TG: 0.5 mg PE, 10.7 mg $K_2Cr_2O_7$. 1 : 5 DSC: 2.27 mg PE, 24.5 mg $K_2Cr_2O_7$, TG: 0.88 mg PE, 8.6 mg $K_2Cr_2O_7$. 1 : 1 DSC: 2.23 mg PE, 4.77 mg $K_2Cr_2O_7$; TG: 2.9 mg PE, 6.25 mg $K_2Cr_2O_7$.

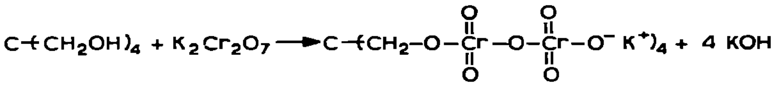
Fig 4. DSC (———) and TG (- - - - - -) curves of pentaerythritol—$K_2Cr_2O_7$ mixtures in air.
1 : 10 DSC: 2.27 mg PE, 46.7 mg $K_2Cr_2O_7$; TG: 0.21 mg PE, 4.68 mg $K_2Cr_2O_7$. 1 : 5 DSC: 2.22 mg PE, 24.2 mg $K_2Cr_2O_7$, TG: 0.44 mg PE, 4.70 mg $K_2Cr_2O_7$. 1 : 1 DSC: 2.21 mg PE, 4.79 mg $K_2Cr_2O_7$; TG: 3.45 mg PE, 7.45 mg $K_2Cr_2O_7$.

completely in the liquid state, the curves for a specific mole ratio differ considerably between the two atmospheres. In air the weights of the final products of the 1 : 10 and 1 : 5 mole ratio mixtures were exactly equal to the weights of $K_2Cr_2O_7$ originally present. In nitrogen the weights of the final products corresponded to the formation of four moles of $K_2Cr_2O_6$ for each mole of PE involved in the reaction. It is assumed that at 450—500°C all the organic material in these mixtures had decomposed and volatilized and that, in air, the reduction product of $K_2Cr_2O_7$ was oxidized back to $K_2Cr_2O_7$.

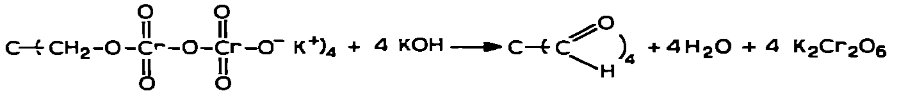
In all the mixtures, infrared spectra indicated the formation of carbonyl groups at about 160°C and, although spectra obtained at higher temperatures were of poor resolution, it appears that carbonyl groups were present over a temperature range of at least 100°C. Furthermore, chromatographic peaks 4 and 5 became very small and peak 1 was much less intense than that of pure PE.

In all samples the onset of an endothermic reaction at about 160°C was observed. The extent to which this reaction occurred prior to the PE phase change increased with increasing reactant mole ratio, as indicated by the relative areas of the phase change peaks, and was found to increase with decreasing heating rate (to 2°C min^{-1}). In all cases this initial reaction was complete at 210°C, below which temperature the decomposition of PE, itself, was insignificant. In the 1 : 10 and 1 : 5 mole ratio samples the weight loss in this temperature range corresponds to the evolution of four moles of water per mole of PE. In the 1 : 1 mole ratio samples it corresponds to the evolution of 2.5 moles of water per mole of PE.

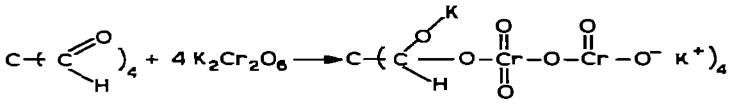
Assuming the existence of chromate ester intermediates, generally accepted as involved in the oxidation of alcohols by Cr(VI), it is possible to represent this reaction in the 1 : 10 and 1 : 5 mole ratio samples by the following steps:



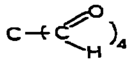
$$C\left(CH_2OH\right)_4 + K_2Cr_2O_7 \longrightarrow C\left(CH_2-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O^-\ K^+\right)_4 + 4\ KOH \qquad (1)$$



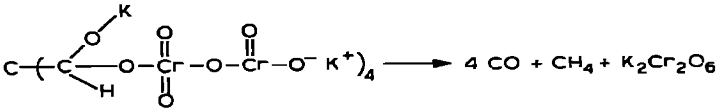
(2)



(3)

The independent existence of  at 210°C is unlikely and, therefore, it is presumed that step 3 began before the completion of step 2. However, it appears that step 3 was slow and was not complete until temperatures considerably greater than 210°C were attained. The rate of completion depended on both the atmosphere, as noted subsequently, and the mole ratio. The amount of unreacted $K_2Cr_2O_7$ available for step 3 was insufficient; yet, in a given atmosphere, the curves for the 1 : 5 and 1 : 10 mole ratio samples are virtually identical. For this reason it is inferred that step 3 involved $K_2Cr_2O_6$ and not $K_2Cr_2O_7$.

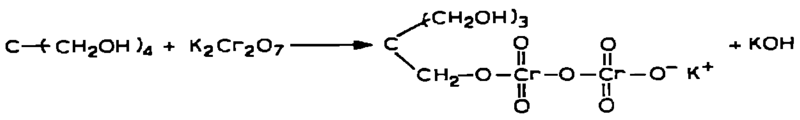
At temperatures greater than 210°C a slow weight loss, somewhat exothermic in nitrogen and highly exothermic in air, was observed. It is believed that this manifests gradual decarbonylation occurring simultaneously with step 3 and represented as step 4



(4)

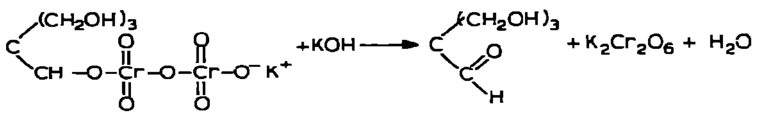
In support of this inference, it is noted that the attendant oxidation of CO to CO_2 would be consistent with the more highly exothermic character of this reaction in air. Furthermore, the formation of CO_2 would be expected to enhance the rate of both step 4 and step 3. In fact, it appears that in air step 4 was complete at about 320°C whereas in nitrogen it was not complete until after the melting of excess $K_2Cr_2O_7$. The broad, exothermic peaks in air between 300 and 380°C are taken to arise from the conversion of $K_2Cr_2O_6$ to $K_2Cr_2O_7$.

The curves for the 1 : 1 mixtures suggest a somewhat different mechanism. Firstly, as noted previously the weight at 210°C corresponds to the loss of 2.5 moles of water per mole of PE. Secondly, the final product in air corresponds to $K_2Cr_2O_4$ (or $K_2O + Cr_2O_3$); no stable species was formed in nitrogen. Thirdly, a very highly exothermic reaction occurred in air between 320 and 360°C. It is postulated that the initial reaction was

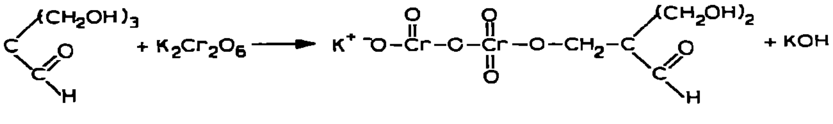


(5)

The following sequence subsequent to step 5 is at least possible



(6)



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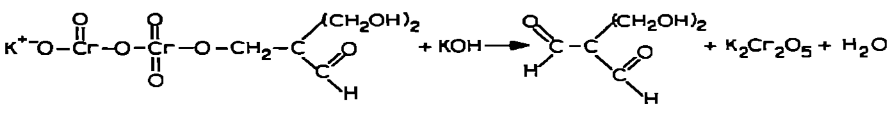

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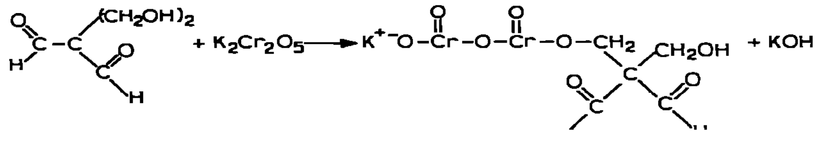
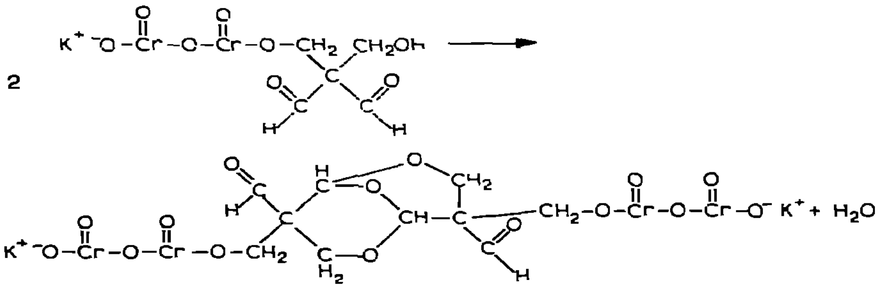


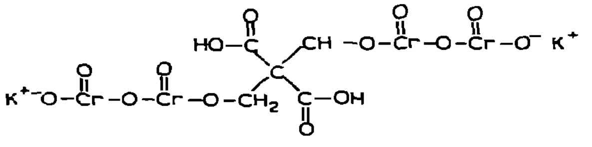
(9)

Steps 5—9, inclusive, account for the loss of two moles of water per mole of PE. Inasmuch as the simultaneous presence of alcohol and aldehyde groups favors the formation of acetals and since the TG data indicate the loss of an additional 0.5 mole of water per mole of PE, the formation of the cyclic acetal shown in step 10 is inferred


(10)

In all probability the remaining aldehyde groups were oxidized to carboxylic acid groups in air, and perhaps even in nitrogen, and the product of step 10 should include the latter.

A slow decomposition, apparently comprising two steps, occured in air between 210°C and 365°C, at which temperature an intermediate corresponding to the following formula was formed

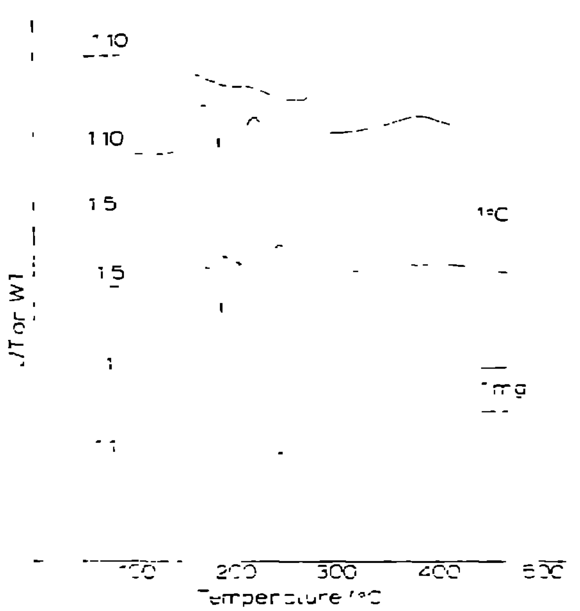


Finally, the loss of all remaining organic material occurred between 365 and 470°C. It is assumed that a cyclic acetal was produced in nitrogen but that in the latter atmosphere its decomposition was so slow that no meaningful intermediates could be observed.

Pentaerythritol and potassium permanganate

The DSC and TG curves of mixtures of PE and $KMnO_4$ are given in Figs. 5 and 6. In no case can the final weights be used in the interpretation of these reactions because of the decomposition of $KMnO_4$ which occurred at 275°C. It was found that $KMnO_4$ formed several decomposition products even when studied as the pure material and in a single atmosphere. In nitrogen, for example, pure $KMnO_4$ was observed to lose from 12.5 to 24% of its weight at 275°C.

Unlike the initial reaction in the PE—$K_2Cr_2O_7$ mixtures, the initial reaction in these samples was exothermic. On the other hand, data obtained by TG, infrared spectrophotometry, and gas chromatography suggest the same reactions as in the $K_2Cr_2O_7$ mixtures. In consequence, it is believed that in the 1 : 10 and 1 : 5 mole ratio samples the initial reaction involved steps such as those proposed as steps 1, 2, and 3 for the $K_2Cr_2O_7$ mixtures and



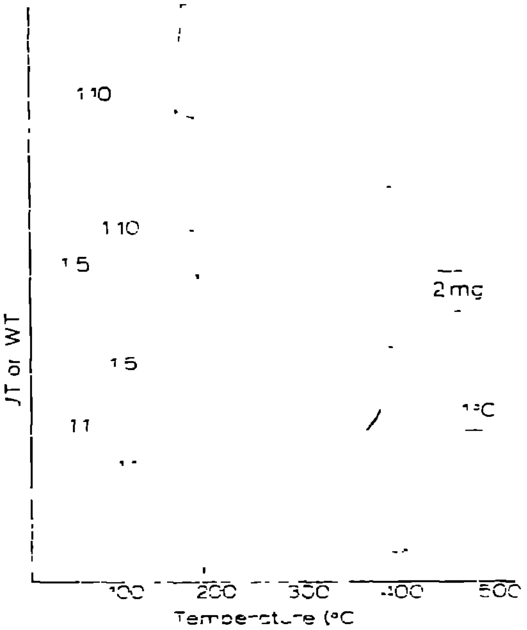
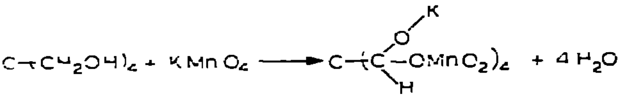


Fig. 5. DSC (———) and TG (------) curves of pentaerythritol—KMnO$_4$ mixtures in nitrogen
1 : 10 DSC: 1 95 mg PE, 22.85 mg KMnO$_4$; TG 0 87 mg PE, 10 17 mg KMnO$_4$. 1 : 5 DSC. 1.97 mg PE, 11 13 mg KMnO$_4$, TG 1.4 mg PE, 8.0 mg KMnO$_4$. 1 . 1 DSC: 1 99 mg PE, 2.31 mg KMnO$_4$; TG: 4 85 mg PE, 5 65 mg KMnO$_4$

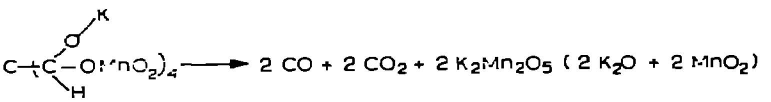
Fig. 6. DSC (———) and TG (------) curves of pentaerythritol—KMnO$_4$ mixtures in air
1 : 10 DSC 3.14 mg PE, 34.3 mg KMnO$_4$; TG: 0.83 mg PE, 9 12 mg KMnO$_4$ 1 : 5 DSC 3.11 mg PE, 18.0 mg KMnO$_4$, TG: 1 5 mg PE, 8 7 mg KMnO$_4$ 1 1 DSC 3 10 mg PE, 3.6 mg KMnO$_4$, TG. 5 0 mg PE, 5.8 mg KMnO$_4$

summarized as step 11



$$C(CH_2OH)_4 + KMnO_4 \longrightarrow C\left(\underset{H}{\overset{OK}{C}}-OMnO_2\right)_4 + 4\,H_2O \qquad (11)$$

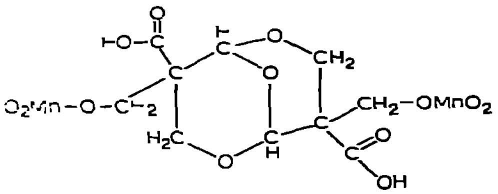
Because the decomposition which ensued was more highly exothermic in air than in nitrogen it is felt to have involved decarbonylation. However, since in nitrogen it was more highly exothermic than the corresponding step in the $K_2Cr_2O_7$ samples and since simple decarbonylation would lead to a product including manganese in the unlikely +5 oxidation state, simultaneous decarboxylation is suggested and a reaction such as that shown as step 12 is proposed



$$C\left(\underset{H}{\overset{OK}{C}}-OMnO_2\right)_4 \longrightarrow 2\,CO + 2\,CO_2 + 2\,K_2Mn_2O_5\ (2\,K_2O + 2\,MnO_2) \qquad (12)$$

Whatever the nature of this decomposition step, it is clear that it occurred more rapidly than the decomposition of the chromate esters. It is possible that, as with $K_2Cr_2O_7$, the initial esterification step was endothermic but that this characteristic was obscured by the relatively early onset of the decomposition.

Surprisingly, in the 1 : 1 mole ratio mixtures the initial reaction with $KMnO_4$ is markedly slower than with $K_2Cr_2O_7$. Breaks in the TG curves at about 210°C indicate the loss of 2.5 moles of water per mole of PE. At higher temperatures little information can be gleaned from the reaction in nitrogen. In air the weight of an intermediate at 370°C and a large exotherm between 370 and 420°C lead to the postulation of a cyclic acetal, probably formed by much the same mechanism as that proposed in the $K_2Cr_2O_7$ study. The formula which follows is proposed



The decomposition and volatilization of all organic material was complete at 415°C.

ACKNOWLEDGEMENT

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