a mixture of 2,6-dimethyloctane (50%) and 2,7-dimethyloctane (50%). A 9 m column of Polyphenylether (10%) on Diasolid L at a temperature of 75 °C with helium as the carrier gas (40 ml/min) was used.

Dimerization of Isoprene with Lithium Dispersion

From 0.1 mole of lithium dispersion, 0.01 mole of *t*-butylamine and 0.1 mole of isoprene, 2.5 g of isoprene dimer mixture were obtained. It was shown by g.l.c. to be a mixture of 2,6-dimethyl-2,6-octadiene and 2,7-dimethyl-2,6-octadiene.

Infrared Absorption Spectra

These were measured on a Koken IRS spectrophotometer, using liquid films.

Nuclear Magnetic Resonance Spectra

These were determined on a Japan Electron Optics Lab. instrument (60 Mc.p.s.) with carbon tetrachloride solutions and with tetramethylsilane as an internal standard.

Acknowledgment

The authors thank Dr. Sanae Tanaka of Mitsubishi Petrochemical Co., Ltd., for providing materials and for measurements of the nuclear magnetic resonance spectra.

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Optimum temperatures in pyrolysis gas chromatography

Russell Sutton[1] and W. E. Harris
Department of Chemistry, University of Alberta, Edmonton, Alberta

Received December 29, 1967

Pyrograms were recorded for a variety of compounds pyrolyzed in the gas phase in a quartz tube. The lowest temperature at which the major pyrolytic products are first formed and the lowest temperatures causing complete pyrolysis were determined and found to differ by about 80–120 °C. The temperatures of complete pyrolysis at the described experimental conditions are 600–650 °C for the most stable compounds. At temperatures above 700 °C the compounds were degraded primarily to methane, ethane, ethylene, or carbon.

Canadian Journal of Chemistry, 46, 2623 (1968)

The temperature of pyrolysis in gas phase pyrolysis gas chromatography (p.g.c.) is of primary importance in obtaining a pyrogram that is characteristic of a reactant. A temperature causing complete pyrolysis is desirable, if the structurally significant products are not also destroyed. The reactant peak in a pyrogram would be of some value for identification, but the retention time of a reactant would usually be prohibitively longer than retention times for the lower molecular weight products. Temperatures and products of pyrolysis of a number of compounds are determined here. Comparisons are made of the results of p.g.c. obtained over a range of temperatures.

Results

The apparatus was previously described (1). Briefly, samples were passed through a gas chromatographic column at 75 °C (to remove air) and then into a heated 3 mm internal diameter 4.7 ml quartz spiral to bring about pyrolysis. The pyrolysis mixture was then sent to a Porapak Q column that was held at 100 °C for 10 min, and then programmed to about 210 °C during a period of 30 min. The helium flow through the pyrolysis tube was 8 ml/min. The sample residence time in the pyrolysis tube was calculated as described elsewhere (1) and found to be 15 s. Calculations with Rummen's (3) equations indicates that the heat transfer in the pyrolyzer was such that the sample was raised to wall temperature in about 6 s.

The products accounting for the major peaks (areas greater than 1% of the total area of all peaks in the pyrograms) were identified from retention times and mass spectra (Table I). Though methane, ethylene, and ethane are usually omitted, they are produced by nearly all compounds and only in exceptional cases are they important for identification. For example,

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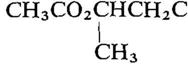
[1] Present address: Department of Chemistry, Knox College, Galesburg, Illinois.

TABLE I

Temperature ranges and products of pyrolysis for several substances

Substance pyrolyzed	Pyrolysis temperature range (°C)*	Major pyrolysis products	
$CH_3CO_2C(CH_3)_3$	280–340	$CH_2=C(CH_3)_2$	CH_3CO_2H
$(CH_2=CHCH_2)_2O$	340–440	$CH_3CH=CH_2$	$CH_2=CHCHO$
 $CH_3CO_2\underset{\substack{\vert \\ CH_3}}{C}HCH_2CH_3$	360–460	$CH_3CH_2CH=CH_2$ CH_3CO_2H	$CH_3CH=CHCH_3$ (*cis* and *trans*)
$CH_2=CHCH_2OCH_2CH_3$	380–480	$CH_3CH=CH_2$	CH_3CHO
$HCO_2(CH_2)_3CH_3$	400–500	$CH_3CH_2CH=CH_2$	HCO_2H
$CH_3CO_2CH_2CH_2CH_3$	420–500	$CH_3CH=CH_2$	CH_3CO_2H
$CH_3CO_2CH_2CH_3$	420–520	$CH_2=CH_2$	CH_3CO_2H
$HCO_2CH_2CH_2CH_3$	420–520	$CH_3CH=CH_2$	HCO_2H
$CH_3CO_2CH(CH_3)_2$	430–530	$CH_2=C(CH_3)_2$	CH_3CO_2H
$HCO_2CH_2CH=CH_2$	460–580	$CH_3CH=CH_2$	CO_2
$CH_3CH_2CO_2CH_2CH=CH_2$	480–580	$CH_3CH=CH_2$	CO_2,$CH_3CH_2CO_2H$
$[(CH_3)_2CH]_2O$	540–640	$CH_3CH=CH_2$ $CH_3CHOHCH_3$	CH_3COCH_3
$CH_3COCH_2CH_3$	540–640	$CH_2=CH_2$ CO	CH_3CH_3
$CH_3CHOHCH_3$	440–640	$CH_3CH=CH_2$	CH_3COCH_3
$(C_2H_5)_2O$	520–660	$CH_2=CH_2$ CH_3CHO	CH_3CH_2OH
$(CH_3CH_2CH_2)_2O$	560–660	$CH_3CH=CH_2$	CH_3CH_2CHO
CH_3CH_2CHO	560–660	CH_3CH_3 $CH_2=CH_2$	CO

*The temperature range includes the lowest temperature at which products are detectable (corresponding to about 1% decomposition) and the temperature at which there is virtually complete pyrolysis (99% reacted).

the ethylene peak would be important to the detection of ethyl acetate pyrolyzed at 500 °C, but of lesser significance when found in the high-temperature pyrogram of *n*-butyl formate. Minor products, usually one to three in number, were not identified. Carbon is also often a product and becomes visible when it accumulates through extended use of a pyrolysis tube.

In Table I the lower temperature listed is that at which the major products were first detectable, where pyrolysis was about 1%. The upper temperature is that at which there was virtually complete pyrolysis and is the temperature at which the reactant peak area was about 1% of the total area for all peaks. The lower and upper limits are valid to about the nearest 10 °C. Note that the upper temperature limits are lower than the temperature required for pyrolysis in stainless steel tubes (2). This lower temperature may be in part due to different residence times and in part because of the use of quartz rather than stainless steel (1). It should be noted further that major products listed in Table I were still present at temperatures up to 600 °C.

The relative amounts of methane, ethane, and ethylene were slightly greater when pyrolysis occurred at the higher temperature, but became significantly greater only above 600 °C. Each of the reactants was degraded to methane, ethylene, ethane, or propylene when pyrolyzed at 700 °C. In addition, water, carbon dioxide, or carbon monoxide accompanied the hydrocarbon products from the oxygen-containing reactants pyrolyzed at 700 °C. For example, isobutyl acetate was converted to acetic acid and isobutene between 430 and 600 °C. Pyrolysis at 700 °C yielded methane, carbon dioxide, ethylene, ethane, and propylene. Acetic acid was then absent from the pyrogram, and the area of the isobutene peak was only one quarter of the area of the same peak formed at 600 °C.

Propionaldehyde and methyl ethyl ketone are a pair of compounds that yield the same major products on pyrolysis. Tertiary and isobutyl acetates are a similar pair. Identification of such materials can be achieved in several ways, such as by measuring relative peak areas or by considering the retention characteristics of the reactants with either a pre-pyrolysis or post-pyrolysis gas chromatographic column. When a chromatographic column is followed with a pyrolysis unit, which in turn is connected to a second column, a nonreactive internal standard such as benzene can aid in the interpretation of retention information. For example, if a mixture of tertiary and isobutyl acetates is injected into a column, the isobutyl acetate will reach the pyrolyzer first, and consequently the isobutene resulting from the isobutyl acetate will slightly precede the isobutene from the *t*-butyl acetate. If benzene is also injected into the mixture, the difference in time of appearance of the two isobutene peaks can be easily fixed with reference to the benzene peak.

Discussion

The pyrolysis of a compound in p.g.c. is more extensive than the 1 to 5% decomposition occurring in many mechanistic studies of pyrolysis (e.g. ref. 4) but the products observed have not differed. Slight pyrolysis of propionaldehyde (4) and isobutane (5) yields the products observed in p.g.c. (1) (Table I). Pyrolytic conversions of ethers to olefins, alcohols, aldehydes, and ketones (6) of esters to olefins and acids, and isopropyl alcohol to acetone and propylene, are well known organic reactions that occur under a variety of conditions used for synthesis and identification. The chain rearrangements accompanying pyrolysis with a catalyst evidently do not occur in non-catalytic homogeneous pyrolysis for p.g.c. The products (pyrogram) for the compounds in Table I are, therefore, characteristic. For example, *t*-butyl acetate and *sec*-butyl acetate yield products (pyrograms) that permit an unequivocal distinction between the two compounds. Generally therefore the structures of the products are related to those of the reactants.

The temperatures (Table I) of pyrolysis in p.g.c. have been found to be comparable to those that are effective in other experimental conditions. Ritchie (7) found that simple carboxylic acid esters pyrolyze at 400–500 °C; ethers (6) have been pyrolyzed at 500–600 °C and propionaldehyde (4) at 400–600 °C.

Acknowledgment

Financial support to Russell Sutton by the National Research Council of Canada is gratefully acknowledged.

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Reactions of 1,2-dichlorohexafluorocyclopentene with secondary phosphines

Richard F. Stockel
Research and Development, Organic Chemicals Division, American Cyanamid Company, Bound Brook, New Jersey 08805

Received February 15, 1968

Dicyclohexylphosphine and diphenylphosphine react with 1,2-dichlorohexafluorocyclopentene to give almost exclusively the monoderivative via displacement of a vinylic chlorine atom. With the former phosphine a disubstituted derivative is also found. In addition to analytical values and infrared spectroscopic data, both ^{19}F and ^{31}P nuclear magnetic resonance spectra support the proposed structures.

Canadian Journal of Chemistry, 46, 2625 (1968)

Introduction

The reaction of 1,2-dichlorohexafluorocyclopentene with various nucleophiles has been studied extensively. With amines (1) and alcohols (2) the products are either C-1 monosubstituted or C-1,3,3 trisubstituted depending on the amount of reactant and the reactivity of the nucleophile. A new reaction path was observed with phosphites, phosphonites, and phosphinite esters with displacement of both chlorine atoms to give exclusively tetraalkylperfluoro-1-cycloalken-1,2,-ylenediphosphonates (3).

The explanation why the monosubstituted derivative was not formed with these phosphorus compounds was rationalized by a reversal of the polarization of the double bond. Therefore, C-2 becomes partially positive and subsequently becomes susceptible to nucleophilic attack. This