[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WAYNE UNIVERSITY AND THE UNIVERSITY OF MARYLAND]

Pyrolysis of Esters. VII. Influence of Acid Portion[1,2]

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Received February 2, 1956

In order to determine the effect of changes in the acid portion of esters on the pyrolysis, a series of twelve esters of methylisobutylcarbinol were pyrolyzed under identical conditions. It was found that the extent of pyrolysis is directly related to the pK_α of the corresponding acid. The methyl carbonate ester was superior to the acetate in those esters that undergo serious side reactions at high temperatures. In most cases, however, the pyrolysis of the acetate is preferred for the production of olefins.

Since the time Smith[5] found that esters could be cleaved by heat, the pyrolysis of esters has been a useful synthetic tool. Kraft[6] developed a method for the preparation of olefins by the distillation of high-boiling esters. Since the ester must have a boiling point above the pyrolysis temperature, only those esters that contain a rather large acid or alcohol moiety are successfully pyrolyzed in this manner. Esters most commonly used in this liquid-phase pyrolysis are those of palmitic,[6] stearic,[7] anthraquinone-β-carboxylic,[8] and benzoic[9] acids. Other esters that also have been pyrolyzed in the liquid phase are those of formic,[10] acetic,[11] chloroacetic,[12] ethyl carbonic,[17] oleic,[7] *p*-methoxybenzoic,[12] *p*-nitrobenzoic,[12] 2,4,6-triethylbenzoic,[13] 2-naphthoic,[14] 2-naphthyl carbonic,[15] *d*-camphoric,[16] *N*-phenylcarbamic,[17] *N*-benzylcarbamic,[18] *N*,*N*-diphenylcarbamic,[12] and methyl trithiocarbonic[17] acids. The Chugaev decomposition of xanthate esters is a closely related reaction.[19] However, since there always is acid present in the liquid phase, rearrangements are common. For example, Manjunath and Plant[20] pyrolyzed 9-acetyl-10-acetoxy-11-hydroxy-6-methylhexahydrocarbazole to obtain, as the only product, 6-acetyl-9-methyl-4-indoxylspiropentane by a pinacol rearrangement. Thus this liquid-phase pyrolysis is most useful for the preparation of acid insensitive olefins or for application in those cases, such as in the steroid field, in which the rearrangement products can be removed from the solid olefin by recrystallization.

In an attempt to avoid rearrangement, Whitmore and Rothrock[21] pyrolyzed pinacoyl acetate to *tert*-butylethylene by passing the vapors through a hot tube containing inert packing. Since that time many sensitive olefins have been prepared by this procedure. It has been shown that, if carbonization is avoided during the vapor-phase pyrolysis, highly strained dienes, such as 1,2-dimethylene-4-cyclohexene,[22] an isomer of *o*-xylene, can be prepared in a 92% yield. The acetates have been used most frequently in these pyrolyses since they are cheap, usually are liquids, and are easy to prepare. However, the esters of the following acids also have been pyrolyzed in the vapor state: formic,[23] propionic,[24] butyric,[23] isobutyric,[25] chloroacetic,[23] phenylacetic,[26] benzoic,[27] methyl carbonic,[27] ethyl carbonic,[27] phenyl carbonic,[27] acrylic,[28] methacrylic,[28] crotonic,[28] α-acetoxypropionic,[29] methyl phthalic,[30]

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[1] Previous paper in this series, *J. Am. Oil Chemists Soc.*, **33**, in press (1956).

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caproic,[31] capric[31], lauric,[31] myristic,[31] palmitic,[31] stearic,[31] β-ethoxyacetic,[31] and 2,4,6-trimethylbenzoic[31] acids. In addition, the symmetrical esters of the dibasic acids, carbonic,[27] glutaric,[31] and phthalic,[24] have been pyrolyzed in the vapor state.

Even though esters of such a large number of acids have been pyrolyzed, there exists no comprehensive information concerning the influence of this acid portion on the ease or extent of pyrolysis of various esters. It seemed reasonable that some of these esters would be more suitable than the acetates for vapor-phase pyrolysis.

For this reason, 12 esters of methylisobutylcarbinol were prepared and pyrolyzed by the dropwise addition of the liquid esters through a Vycor tube packed with $^1/_8$-inch Pyrex helices. The methylisobutylcarbinol was chosen because it was readily available, formed liquid or low-melting esters, and produced a relatively stable olefin in a convenient boiling range. The acetate was selected as the standard of comparison. The tube was externally heated at 450° and the system was continuously flushed out with oxygen-free nitrogen. By the use of these standard conditions, the acetate eliminated 68% of the theoretical amount of acetic acid.[32] Under these rather mild conditions no carbonization that could promote an acid-catalyzed elimination reaction occurred in the tube.[22] Since the extent of pyrolysis is strongly dependent on the rate of addition, the temperature of the column, and the rate of flow of nitrogen, the acetate was pyrolyzed at frequent intervals throughout these studies to ensure that the experimental conditions were constant.

Under these standard conditions the methylisobutylcarbinol esters of propionic and butyric acids eliminated 68% of the theoretical amount of the corresponding acid and those of isovaleric, heptanoic, and pivalic acids eliminated 67%. It appeared from the results of the pyrolysis of these esters that little or no effect was produced by an increase in the length of the alkyl group of the aliphatic acids. Even steric hindrance is not an important factor since the pivalic ester, which has three methyl groups to hinder the reaction, pyrolyzes to almost the same extent as does the acetate. This observation is in agreement with the fact that ethyl 2,4,6-trimethylbenzoate can be converted to the corresponding hindered acid in 90% yield by pyrolysis at 560°.[31] Fuson and Hammann found that steric factors are not extremely important in the formation of internal rings.[33] Because of the small effect of the alkyl groups of the carboxylic acid, the higher aliphatic esters were not studied. It can be assumed that the palmitates and stearates would not differ substantially from the acetate or heptanoate, in extent of pyrolysis.

When the chloroacetate of methylisobutylcarbinol was pyrolyzed under the standard conditions, 87% of the theoretical amount of chloroacetic acid was liberated. In contrast with alkyl groups, the electronegative chlorine atom has a marked effect. This would indicate that the chloroacetate would be superior to the acetate for the synthesis of olefins. However, it has not been determined how effective the stronger chloroacetic acid would be for the promotion of the rearrangement of the resulting olefins. Presumably the use of the chloroacetate would be advantageous for the preparation of olefins, such as methyl acrylate, that are relatively insensitive to acids.

The benzoate, under these same pyrolytic conditions, liberated 73% of the theoretical amount of the benzoic acid. The disadvantage of the presence of the solid benzoic acid in the pyrolysis apparatus counterbalances the increased conversion compared to the acetate. The *p*-methoxybenzoate, which has an electron-releasing methoxyl group, eliminated only 71% of the theoretical amount of the acid under these standard conditions while the *p*-chlorobenzoate, which has the electron-withdrawing chloro group, eliminated 77%. When the *p*-nitrobenzoate was used, 93% of the theoretical amount of acid was liberated but the reaction could not be carried out without extensive carbonization.

There appears to be a correlation between the acidity of the acid portion of the ester and the extent of pyrolysis under these standard conditions. If the dissociation constant of the acid is plotted against the per cent of pyrolysis for each of the methylisobutylcarbinyl esters, the points fall along a straight line (Fig. 1). Only the data for *p*-nitrobenzoic acid, which undergoes extensive carbonization, do not fall near the line. This is additional evidence that the carbon deposit promotes an acid-catalyzed elimination reaction during the pyrolysis.

In a separate experiment to test the effect of carbonaceous deposits on the extent of pyrolysis, the methylisobutylcarbinyl acetate was pyrolyzed through a tube containing a black carbon deposit. Under these conditions, 83% of the theoretical

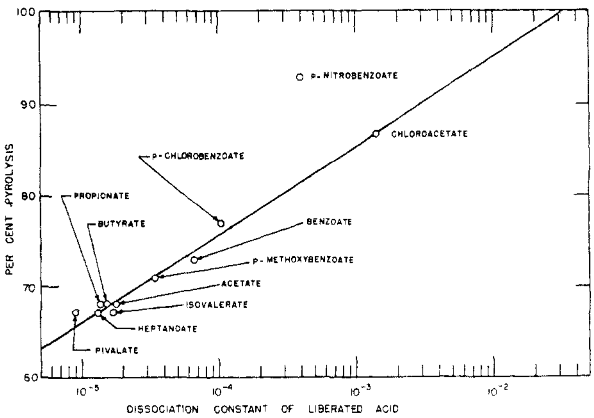

FIGURE 1

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(31) Bailey and Turek, *J. Am. Oil Chemist's Soc.*, **33**, in press (1956).

(32) Bailey and King, *J. Am. Chem. Soc.*, **77**, 75 (1955).

(33) Fuson and Hammann, *J. Am. Chem. Soc.*, **74**, 1626 (1952).

amount of acetic acid was eliminated, compared to the 68% obtained in the absence of carbon. One must conclude that the deposit catalyzes an elimination reaction (presumably by acid catalysis) that proceeds faster than the usual unimolecular cyclic mechanism of ester pyrolysis. Houtman, van Steenis, and Heertjes[34] even explained the fact that their primary esters did not decompose at 500° unless a carbon deposit was present by assuming that the acidic carbon deposit was necessary for the pyrolysis of all esters.

Nace and O'Conner,[35] in their recent study on the Chugaev reaction, found that in the decomposition of the xanthates, $RS\text{-}\overset{\overset{S}{\|}}{C}\text{—}OR'$, the plot of the rate of decomposition *versus* the dissociation of the related acid, $R\text{-}\overset{\overset{O}{\|}}{C}\text{—}OH$, formed a straight line. It is extremely interesting that the introduction of a sulfur atom between the R and the carboxyl group or presence of the carbon-to-sulfur double bond does not affect this straight-line relationship. This relationship would suggest that esters of a strong acid such as trifluoroacetic would pyrolyze very easily. However, the strong acid that is formed may promote acid-catalyzed elimination or rearrangement. For this reason, the use of esters of weakly acidic aliphatic esters will probably ensure that elimination will proceed by only an intramolecular cyclic mechanism. Therefore, because acetates are easy to prepare, are usually liquids and produce liquid products, are relatively low molecular weight and inexpensive, and because the liberated acetic acid is a relatively weak acid, the acetates will continue to be the most popular ester for pyrolysis.

One ester that may have some special use to avoid acid-catalyzed rearrangements at a slightly lower temperature of pyrolysis than that necessary for the pyrolysis of acetates is the methyl carbonate. These esters are easily prepared by reaction of methyl chloroformate and the alcohol in pyridine.[36] Under the same conditions that resulted in the elimination of 68% of the theoretical amount of acid from the acetate, the methylisobutylcarbinyl methyl carbonate liberated 92% of the theoretical amount of carbon dioxide. The course of the reaction also is convenient to follow by the absorption of the liberated carbon dioxide in an Ascarite tube. Since the products of the pyrolysis, methyl alcohol and carbon dioxide, are relatively nonacidic, the methyl carbonate ester should be of use in the preparation of highly reactive olefins. The comparison of the two esters (Table I) shows that the methyl

TABLE I

PROPERTIES OF METHYLISOBUTYLCARBINOL ESTERS

Ester of Methylisobutylcarbinol	Boiling Point °C.	Boiling Point Mm.	n_D^{25}	d_{25}^{25}	Analysis Calc'd C	Analysis Calc'd H	Analysis Found C	Analysis Found H	Acid Derivative Used for Esterification	Reflux, Hr.	Yield, %	Extent of Pyrolysis at 450°, %
Acetate	145.5–146.5[a]	735	1.3988	0.8548	64.82	10.82	64.90	11.01	Acetic anhydride	12	97	68
Propionate	163.5–163.6	742	1.4051	0.8542	68.31	11.46	68.11	11.33	Propionyl chloride	0.1	90	68
Butyrate	83.4–83.5	23	1.4097	0.8504	69.70	11.70	69.61	11.86	Butyryl chloride	0.1	90	69
Isovalerate	84	16	1.4102	0.8441	70.92	11.90	70.70	12.09	Isovaleryl chloride	0.1	90	67
Pivalate	100	60	1.4045	0.8336	70.92	11.90	71.10	11.73	Pivalic acid	60	73	67
Heptanoate	83	2	1.4234	0.8482	72.83	12.23	72.61	12.16	Heptanoyl chloride	0.1	80	67
Chloroacetate	132.5–133.0	102	1.4287	1.0125	53.72	8.46	54.00	8.65	Chloroacetyl chloride	0.1	89	87
Benzoate	98	2.2	1.4863	0.9662	75.68	8.79	75.49	8.71	Benzoyl chloride	0.1	80	73
p-Chlorobenzoate	104.5	0.7	1.5025	1.0645	64.86	7.12	64.87	7.23	*p*-Chlorobenzoyl chloride	0.1	70	77
p-Methoxybenzoate	131	1.5	1.5036	1.0140	71.15	8.53	71.43	8.27	*p*-Methoxybenzoic acid	96	85	71
p-Nitrobenzoate	146	1.6	1.5094	1.1104	62.13	6.82	61.95	7.11	*p*-Nitrobenzoyl chloride	1	72	93[b]
Methyl carbonate	109.5–110.0	19	1.4019	—	59.97	10.06	60.27	10.14	Methyl chloroformate	48	89	92[c]

[a] Reported[38] b.p. 147–148°. [b] Considerable charring occurred. [c] At 400°, only 43% of the theoretical amount of carbon dioxide was liberated and at 350°, less than 1%.

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(34) Houtman, van Steenis, and Heertjes, *Rec. trav. chim.*, **66**, 781 (1946).

(35) Nace and O'Conner, *J. Am. Chem. Soc.*, **75**, 2118 (1953).

(36) Bailey, Cunov, and Nicholas, *J. Am. Chem. Soc.*, **77**, 2787 (1955).

carbonate ester decomposes approximately 40° lower than the corresponding acetate.

EXPERIMENTAL[37]

Preparation of esters. Twelve esters of methylisobutylcarbinol were prepared and carefully purified for pyrolysis as listed in Table I. The acetate[38] was prepared from acetic anhydride and methylisobutylcarbinol as previously described.[32] The methylisobutylcarbinyl pivalate and *p*-methoxybenzoate were prepared from the carbinol and the corresponding acid by the use of a benzene solution and a catalytic amount of *p*-toluenesulfonic acid. The water formed in the esterification was removed by a Dean-Stark trap. The reaction mixture was extracted several times with a sodium carbonate solution and was worked up in the usual manner.

The other nine esters were prepared from the carbinol and the corresponding acid chloride. A typical esterification, the preparation of methylisobutylcarbinyl propionate, is described. In all cases only the center cuts which had the physical properties and the analyses listed in Table I were used for the pyrolysis experiments.

Methylisobutylcarbinyl propionate. To mixture of 102 g. (1 mole) of methylisobutylcarbinol and 87 g. (1.10 moles) of anhydrous pyridine was added dropwise with stirring 100 g. (1.08 moles) of propionyl chloride while the temperature of the reaction mixture was kept below 60°. After the addition was complete, the reaction mixture was heated to boiling and immediately cooled. The organic layer was decanted from the pyridine hydrochloride and the salts were dissolved in water. The small amount of organic layer was removed and combined with the original organic layer. The combined organic layers were washed with water, then with a sodium bicarbonate solution followed with water. After the organic solution was dried over sodium sulfate, the crude ester was fractionated through a 12-inch, helix-packed column to yield 142 g. (90%) of methylisobutylcarbinyl propionate, b.p. 163.5–163.6° (742 mm.), n_D^{25} 1.4051, d_{25}^{25} 0.8542.

Pyrolyses of methylisobutylcarbinyl esters. The apparatus used for all the pyrolyses was similar to that previously described.[39] It consisted essentially of a vertical Vycor tube, 25 mm. in diameter and 200 cm. long, equipped with standard taper joints and a side-inlet tube near the top for the introduction of a slow stream of oxygen-free nitrogen. This tube was packed to a depth of 10 inches with $^1/_8$-inch Pyrex helices and externally heated with a Hoskins FD 303A furnace. The temperature was determined with a thermocouple located between the Vycor tube and the furnace. The liquid esters were forced by air pressure from a side-inlet flask through an inverted U-shaped capillary delivery tube to the top of the pyrolysis tube in order to keep the rate of addition as constant as possible. Before each pyrolysis the whole system was flushed for 45 minutes with nitrogen and throughout the pyrolysis the nitrogen was introduced at a rate of 3 ml. per minute.

The acetate was selected as a standard for all pyrolyses. Methylisobutylcarbinyl acetate was pyrolyzed at 450° until reproducible results could be obtained. The other esters were pyrolyzed under conditions as close as possible to those used for the acetate. At periodic intervals throughout the study of the pyrolyses, the acetate was rerun to make certain that the same pyrolytic conditions were being used. The pyrolysis tube was cleaned for each run by hot nitric acid and was thoroughly washed with distilled water.

The extent of pyrolysis of the methylisobutylcarbinyl methyl carbonate was determined by the absorption of the liberated carbon dioxide in an Ascarite tube. The extent of pyrolysis of each of the other esters was determined by titration of the aqueous extracts of the pyrolysate.

In the pyrolysis of methylisobutylcarbinyl *p*-nitrobenzoate considerable carbon formation invariably occurred. In the pyrolyses of all the other esters listed in Table I little or no carbon formation was noted.

In a separate experiment, methylisobutylcarbinyl acetate was dropped through the pyrolysis tube at 500° in the presence of air until the tube was covered with a black carbonaceous deposit. When this tube was used without cleaning for the pyrolysis of methylisobutylcarbinyl acetate at 450° under otherwise standard conditions, 83% of the theoretical amount of acetic acid was liberated.

A typical pyrolysis of the methylisobutylcarbinyl butyrate is described.

Pyrolysis of methylisobutylcarbinyl butyrate. At the rate of 2 g. (0.0116 mole) per minute, 50 g. of methylisobutylcarbinyl butyrate was added to the top of the pyrolysis tube. The pyrolysate was condensed in a 6-inch spiral condenser and collected in a side-inlet flask cooled in a Dry Ice-chloroform-carbon tetrachloride bath. The pyrolysate was extracted with an excess of a cold standard sodium hydroxide solution and then with water until the aqueous washings were neutral to litmus paper. Back titration of the combined standard base and aqueous washings with standard hydrochloric acid indicated that 69% of the theoretical amount of butyric acid had been liberated. The organic layer was dried over sodium sulfate and the dried solution was fractionated through a 6-inch, helix-packed column to yield 15.8 g. (65%) of 4-methyl-1-pentene, b.p. 53–54° (748 mm.), n_D^{25} 1.3805 [reported b.p. 54.0–54.1° (760 mm.),[40] n_D^{20} 1.3820[41]].

DETROIT 1, MICHIGAN
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[37] The authors are indebted to Vivian Kapuscinski for the microanalyses.

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[39] Bailey and Golden, *J. Am. Chem. Soc.*, **75**, 4780 (1953).

[40] Mulliken, Wakeman, and Gerry, *J. Am. Chem. Soc.*, **57**, 1605 (1936).

[41] Schmitt and Boord, *J. Am. Chem. Soc.*, **54**, 751 (1952).