Mechanism of Organic Reactions. IV. Pyrolysis of Esters and Acetals[1,2]

BY EARL M. BILGER AND HAROLD HIBBERT

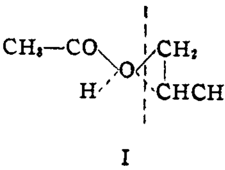
The nature of the carbonyl group and the relative tendency toward migration of hydrogen atoms present in derivatives containing this group play a prominent role in a large number of reactions of biological and industrial importance, more particularly in those relating to carbohydrates. The object of the present investigation was a study of the behavior of this group during the decomposition of esters by heat. The authors aimed to devise a single mechanism for the pyrolysis of all esters, those of inorganic and organic acids; of primary, secondary and tertiary alcohols; of those decomposing smoothly into acids and hydrocarbons; and of those behaving abnormally when heated, showing great stability and, at sufficiently high temperatures, undergoing complex decomposition. Those of the last type lack a β-hydrogen atom in the alkoxy part of the ester.

In attempting to arrive at an explanation of the mechanism of ester decomposition, the theory of the intermediate formation of ethers and their subsequent dehydration was discarded early in the study. It is known[3] that simple ethers are not readily dehydrated to produce olefins and confirmation of this is given in the experimental part.

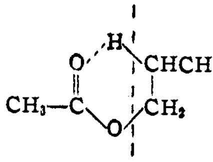
Two further possibilities of the course through which ester decomposition might proceed were considered: (a) intermediate, unstable intracyclic compounds,[4] isomeric with the esters themselves, may be formed; or, (b) a primary dissociation may occur in accordance with the modern radical theory[5] as developed and extended from Nef's earlier ideas on dissociation.[6]

Four possible types of intracyclic intermediates were conceivable, namely, oxonium, chelate, hemi-acetal (5-, 4- or 3-membered) and acetal (6-, 5- or 4-membered)[7] rings.

The case of *n*-propyl acetate may be used in illustration, from which formulas I, II, III and IV, respectively, would represent these four types. The dotted lines indicate the possible position of cleavage to portray the formation of "acid + olefin."



I



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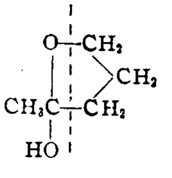
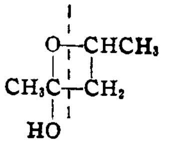
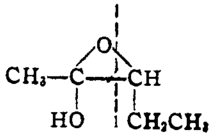


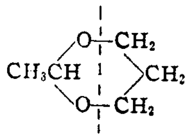
IIIa



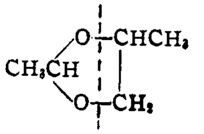
IIIb



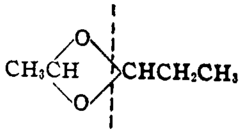
IIIc



IVa



IVb



IVc

It may be seen readily that these types of reactions would account theoretically for the formation of intermediates and subsequently for the final products in the pyrolysis of all types of esters of organic acids.

No study was given to cases I, II or III in the present paper, but case IV, the cyclic acetals, was considered in some detail. Also, investigations pertinent to the problem at hand were made on the relative stability of the esters of primary and secondary alcohols; of ethyl and methyl esters; of isomeric chloro esters and of alkyl halides. Data and discussions are given in the experimental section of the paper. They show conclusively

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(1) Presented at the Washington meeting of the American Chemical Society, April, 1924. Abstracted from the dissertation presented by Earl M. Bilger to the Faculty of the Graduate School of Yale University, June, 1925, in candidacy for the degree of Doctor of Philosophy.

(2) A recent review and discussion of the literature dealing with the pyrolysis of organic compounds is to be found in the publication by Hurd, "The Pyrolysis of Carbon Compounds," Amer. Chem. Soc. Monograph No. 50, Chemical Catalog Co., New York, 1929.

(3) Beilstein, Vol. I, 3d ed., 1893, p. 110.

(4) Sielisch and Grund, "Ueber den Mechanismus intra- und intermolekulare Reactionen (Theorie des Ringtausches)," Verlag Walter Blank, Berlin, 1932.

(5) Gomberg, *Ber.*, **33**, 3150 (1900); Wieland, *ibid.*, **42**, 3029 (1909); Paneth and Hofeditz, *ibid.*, **62**, 1335 (1929); Paneth and Lautsch, *ibid.*, **64**, 2702, 2708 (1931); Rice, THIS JOURNAL, **53**, 1959 (1931); Rice, Johnston and Evering, *ibid.*, **54**, 3529 (1932); Rice, *Chemical Reviews*, **10**, 147 (1932).

(6) Nef, THIS JOURNAL, **26**, 1549 (1904); **30**, 645 (1908); cited by Henrich, trans. Johnson-Hahn, "Theories of Organic Chemistry," 1922, p. 354.

(7) Hill and Hibbert, THIS JOURNAL, **45**, 3108 (1923).

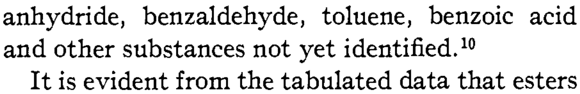
that cyclic acetals are not formed as intermediates in the pyrolysis of the esters studied and provide strong evidence against the formation of this type of ring in any ester decomposition. The experimental evidence indicates the remarkable stability of cyclic acetals at relatively high temperatures.

The authors believe that the modern "radical theory" as first put forward by Nef, and later extended by Rice and co-workers, affords the most probable explanation of changes occurring in the decomposition of all types of esters.

However, unless the radicals concerned are actually isolated and their reactions studied, it is difficult to say which course is followed in forming the known final products of ester decomposition. The important considerations are that free radicals, rather than intermediate unstable cyclic compounds, are formed in the first stage of decomposition, and also that the mechanism of all ester decompositions may be explained by the application of the "radical theory." Lack of space prevents the inclusion of illustrative equations.

The fission may take place either at one or more places in the molecule, for example,

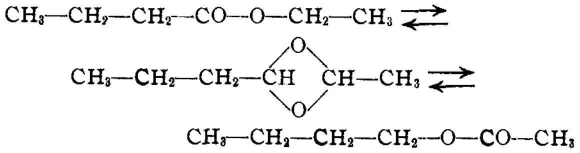
$$CH_3COO \,\vdots\, CH_2CH_2R \longrightarrow CH_3COO- + -CH_2-CH_2-R \longrightarrow CH_3COOH + CH_2{=}CH-R \quad (1)$$



$$C_6H_5CO \,\vdots\, O \,\vdots\, CH_2C_6H_5 \begin{cases} \nearrow C_6H_5CO- + -OCH_2C_6H_5 \\ \searrow C_6H_5COO- + -CH_2C_6H_5 \end{cases} \quad (2)$$

In the first case only the acid and olefin are formed while in the second, as found by Hibbert and co-workers[8] and confirmed later by Hurd and Bennett,[9] the four free radicals can interact to give rise to a number of new products: benzoic anhydride, benzaldehyde, toluene, benzoic acid and other substances not yet identified.[10]

It is evident from the tabulated data that esters of secondary alcohols decompose more readily than do those of primary alcohols. A comparison of the data for the decomposition of ethyl *n*-butyrate and *n*-butyl acetate shows that four-membered acetals are not intermediates in ester pyrolysis. These two esters should give the same intermediate acetal, thus



Contrary to expectation, the data show that the decomposition products are different for the two esters.

It has been pointed out that all esters do not decompose normally into olefins and acids. Thus esters having no β-hydrogen atom in the alkoxy part of the molecule either undergo complex decomposition or show greater stability than ethyl esters. For example, methyl benzoate remained unchanged while the ethyl ester decomposed quantitatively into ethylene and benzoic acid; methyl formate gave no olefin, the ethyl ester 45%; methyl acetate remained unchanged but ethyl acetate was decomposed into ethylene (77%) and acetic acid (77%). Neither benzyl benzoate nor benzyl acetate underwent any decomposition. The marked difference in the behavior of the isomers, ethyl benzoate and benzyl acetate, which should give the same acetal, again provides strong evidence against the theory of four-membered acetal rings as intermediates in the pyrolysis of organic esters.

Experimental Section

In the process of pyrolysis between 19.96 and 23.2 g. of the substance was dropped slowly and at a uniform rate into a volatilizing chamber. The vapors were led into a heating unit which consisted of a quartz tube, 107 cm. long and 1.9 cm. in diameter, 91 cm. of which was wound spirally with high resistant nichrome ribbon. The tube was well insulated and carried a thermocouple. From the approximate volume of the heating zone, 260 cc., the approximate time of contact of the vapor within the hot zone was calculated for each sample pyrolyzed. Carbon dioxide was circulated through the apparatus during the process. Products were isolated by condensation and by absorption in bromine.

Stability of Ethyl Ether.—Two experiments (A and B) were performed with ethyl ether at 486°, the temperature at which ethyl acetate decomposes into ethylene and acetic acid. In (A) 20 g. of it was taken during forty-eight minutes (contact time, 0.74 min.), and in (B) a mixture of 8.4 g. of ethyl ether and 11.6 g. of acetic anhydride was passed through the heated tube in sixty minutes (contact time 1.1 min.). In neither case was there any production of ethylene. The ether recovered from (A) weighed 18.9 g.; the liquids recovered from (B) weighed 17.3 g. In both cases, some ether was found in the bromine water. The data provide evidence against the theory of ether formation, although the results do not preclude the possibility of the formation of ethers as transient intermediates.

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[8] Montonna, Ph.D. dissertation Yale University, 1924; Bilger, Ph.D. dissertation, Yale University, 1925.

[9] Hurd and Bennett, THIS JOURNAL, 51, 1197 (1929).

[10] Considerable further work has been carried out on this reaction by Dr. R. L. Montonna, University of Minnesota, with a view to the identification of the entire reaction products, and it is hoped to publish these results in the near future.

PYROLYSIS OF ESTERS AND ACETALS

Starting material	Temp., °C.	Total time, min.	Time of contact in hot zone, min.	Products obtained Olefins moles[a]	Products obtained Acid moles	% Decomposed into Olefin	% Decomposed into Acid
Ethyl acetate	485	65	1.2	0.174 (E)	0.176	76.6	77.8
Ethylene acetal	485	65	1.2	.023 (E)	.005	10.2	2.3
Ethyl *n*-butyrate	470–478	70	0.15	.139 (E)	.140	69.8	69.5
Ethyl *n*-butyral	470–478	60	.13	.048 (E)	.029	23.8	14.3
Ethyl formate	488	65	1.0	.122 (E)	.026	45.4	9.5[b]
Ethylene formal	474	67	1.2	.008 (E)	.003	3.4	1.1
n-Propyl acetate	470	75	1.6	.097 (P)	.140	49.5	71.5
Propylene acetal	470	80	1.7	.021 (P)	.024	10.9	12.4
Propylene *n*-heptal[c]	486	65	2.3	.040 (P)	.015	33.5	13.2
Trimethylene *n*-butyral	485	80	2.2	.040 (P)	.009	25.3	5.7
n-Butyl acetate	500	60	1.2	.151 (B)	.157	75.7	78.6
i-Butyl acetate	500	60	1.2	.141 (B)	.155	70.7	77.8
s-Butyl acetate	500	60	1.2	.177 (B)	.180	88.5	90.2
i-Propyl acetate	470	65	1.4	.181 (P)	.181	97.4	90.5

[a] E, P, B denote ethylene, propylene and butylene, respectively. [b] Formic acid is readily decomposed. [c] B. p. 204°, unpublished work.

Esters and Acetals.—Seventeen esters and six cyclic acetals were subjected to pyrolysis. Data are recorded in the accompanying table. The first four esters and the first four acetals[11] are isomeric. Unchanged acetals, identified by boiling points, were found in the distillates in quantities which indicated that no decomposition occurred except as shown in the table.

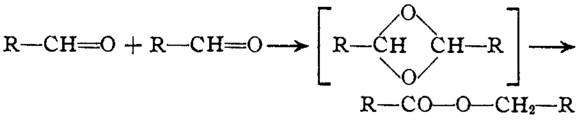
The data prove that cyclic acetals are much more stable than their isomeric esters and provide evidence that six- and five-membered acetals are not intermediates in ester decomposition. By comparing the percentages of the esters converted into olefins and acids, respectively, it is seen that acetal decomposition is a complex reaction and not merely a change into acids and olefins.

Beta-chloroethyl acetate and ethyl chloroacetate were subjected to pyrolysis. The former decomposed to the extent of 38.1% to give monochloroethylene dibromide, b. p. 163°. In the latter case 58.2% decomposed to give ethylene dibromide. Fully halogenated alpha-chloroesters are known to decompose to give acid chlorides.[12] These facts indicate that in ester decomposition the olefin derivative comes solely from the alkoxy portion of the ester.

The pyrolysis of beta-chloroethyl acetate was repeated in the presence of a small amount of chloroacetic acid. In agreement with Konowalow[13] it was found that the pyrolysis was not catalyzed in the gaseous phase.

Nef[14] investigated the pyrolysis of several alkyl halides and found that ethyl bromide decomposed completely into olefin and acid at 500°. The authors find that ethyl bromide decomposes to the extent of 58.7% when pyrolyzed at 482°, while with *n*-butyl bromide the decomposition amounts to 41.6% at 484°, each giving its corresponding olefin. No further study of alkyl halides was made since the investigation of the esters of organic acids appeared to offer a more interesting problem from the standpoint of the nature of the mechanism involved.

The pyrolysis products from all esters investigated were examined for the presence of aldehydes, using an acetic acid solution of *p*-nitrophenylhydrazine. No aldehydes were found, showing that ester decomposition is not a reversal of the Tischtschenko[15] reaction, which the authors assume to proceed thus:



Summary

1. Esters of organic and of inorganic acids have been pyrolyzed in the gaseous state and the products studied qualitatively and quantitatively.

2. Ester pyrolysis does not proceed through intermediates which have ring structures of the acetal type. Cyclic acetals are very much more stable to thermal effects than their isomeric esters.

3. Ester pyrolysis and reverse reactions are best explained by the "radical theory" as developed and extended from Nef's dissociation theory. This assumes a primary dissociation into very reactive radicals containing elements with abnormal valencies.

4. Experimental evidence does not support the idea that ester pyrolysis proceeds through ether intermediates.

5. The stability of isomeric esters toward heat is greater for those derived from primary than from secondary alcohols.

6. Methyl esters, or substituted methyl esters, are much more stable toward heat than either ethyl esters, beta-substituted ethyl esters, or the higher alkyl esters.

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[11] The authors' thanks are due Dr. John Timm and Dr. Harold Hill for a supply of these materials.

[12] Cahours, *Ann.*, **258**, 62 (1890).

[13] Konowalow, *Ber.*, **18**, 2808 (1885).

[14] Nef, THIS JOURNAL, **26**, 1549 (1904); **30**, 645 (1908).

[15] Tischtschenko, *J. Russ. Phys.-Chem. Soc.*, **38**, 355, 482 (1906); *Chem. Centr.*, **77**, 1309, 1552 (1906).

7. In ester decomposition the olefin derivative comes solely from the alkoxy portion of the ester.

8. Ester pyrolysis does not represent a reversed Tischtschenko reaction.

9. The decomposition into acid and olefin by pyrolysis of an organic ester containing hydrogen attached to the β-carbon atom of the alkoxy radical is a general type of reaction.

MONTREAL, CANADA RECEIVED JANUARY 22, 1936

[CONTRIBUTION FROM THE GEOCHEMICAL LABORATORY, ILLINOIS STATE GEOLOGICAL SURVEY]

Formation of Hydrogen Peroxide in the Silver Reductor: A Micro-analytical Method for Iron[1]

BY CHARLES F. FRYLING AND FAY V. TOOLEY

An investigation of the decolorization of silica containing less than 0.1% of ferric oxide indicated the desirability of an accurate and rapid analytical method applicable to small samples. After considering various procedures, that of Walden, Hammett and Edmonds[2] appeared most promising. This method involves reduction of ferric ion in dilute hydrochloric acid by passage over metallic silver followed by titration with standardized ceric sulfate solution using ortho-phenanthroline–ferrous complex as indicator.

The possibility of applying this method depends primarily on the completeness of reduction of ferric ion to ferrous ion by metallic silver. An idea of the extent of reduction can be obtained from theoretical considerations. The ratio of ferrous–ion concentration to ferric-ion concentration at equilibrium can be calculated by substituting the concentration of silver ions given by the solubility product of silver chloride (S_{Ag}) in the expression for the equilibrium constant (K) of the reaction $Fe^{+++} + Ag = Ag^{+} + Fe^{++}$. The numerical values of S_{Ag} and K are commonly recorded as 1.1×10^{-10} and 0.1.

In our analyses, 10 cc. of solution containing approximately 0.0015 g. of ferric ion was diluted to 50 cc. with N hydrochloric acid and passed through the reductor. The concentration of chloride ion [Cl^{-}] was therefore 0.8 M and the initial concentration of ferric ion $[Fe^{+++}]_i$ was 5.38×10^{-4} M. Using the solubility product gives a value of 1.38×10^{-10} for the concentration of silver ion. To simplify the calculation it is accurate to assume that the equilibrium ferrous-ion concentration [Fe^{++}] is equal to the initial concentration of ferric ion. The equilibrium concentration of ferric ion [Fe^{+++}] is therefore calculated as 7.4×10^{-13} and the equilibrium ratio, $[Fe^{++}]/[Fe^{+++}]$, is 7×10^{8}. Since it seems unlikely that significant errors are introduced by neglecting the activities of Ag^{+} and Cl^{-} in the solubility product, the reduction can be considered as proceeding to completion.

First attempts to apply this method employing 0.01 N ceric sulfate solution and a micro buret to samples containing 1.5 mg. of iron (about one-tenth the quantity studied by Walden, *et al.*) yielded exceedingly discordant results. It was found that these discrepancies could be eliminated by applying two corrections: one for the indicator, and, due to the formation of hydrogen peroxide, a reductor correction, which must be reduced to as low a value as possible.

The Indicator Correction

When titrating 1.5 mg. of iron, approximately 5% of the 0.01 N ceric sulfate solution is required to oxidize the indicator from the red to the blue modification. It is therefore necessary to determine the titer[3] of the indicator accurately and to subtract this correction from the titer of the iron solution.

In order to determine this correction, the 0.025 M indicator was diluted to 0.0005 M. Titrations were conducted on measured volumes of the diluted indicator in 100 cc. of 1 N hydrochloric acid. The curve obtained by plotting volume of indicator against its titer (cc. of standardized 0.01 N ceric sulfate) is linear, intersects the origin and the experimental points lie on the theoretical curve drawn for a 0.0005 M solution (Fig. 1). This latter correspondence was unexpected, for

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(1) Published with the permission of the Chief, Illinois State Geological Survey, Urbana, Ill.

(2) Walden, Hammett and Edmonds, THIS JOURNAL, **56**, 350 (1934).

(3) Throughout this paper the term "titer" is used to indicate the volume of standardized solution required for titration.