but are strongly dependent on degree of esterification, being highest for degree of esterification in the range 0.3 to 0.5. Enzyme-deësterified pectins form weaker ionic-bonded gels than do acid-deësterified pectins.

PHILADELPHIA, PA. RECEIVED SEPTEMBER 13, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Allylic Rearrangements. XIX. Studies of the Ozonization of Allylic Systems[1]

BY WILLIAM G. YOUNG, ART C. MCKINNIS, IRVING D. WEBB AND JOHN D. ROBERTS

During the investigation of the reactions of certain allylic systems under controlled conditions it has been necessary to devise methods for the analysis of mixtures of allylic isomers, the compositions of which could not be readily determined by the fractional distillation procedures used previously.[2]

Hurd[3] has applied the ozonolysis method to the analysis of hexenyl bromides and the results are in satisfactory agreement with those obtained by the refractometric method. We have investigated the ozonization of other types of allylic systems giving particular attention to the influence of the group X on the products obtained from isomers of the type RCH=CH—CHR'X(I) and RCHX—CH=CHR' (II).

The general ozonization procedures for compounds of types I and II involve treatment of the unsaturated compound with ozone (taking care to avoid overozonization) followed by hydrolysis[3b] of the ozonide, mild oxidation of the products and analysis of the volatile acids, RCOOH and R'COOH, by the method of Dyer.[4] The procedure gave excellent results with simple compounds such as 2-pentene and 2,4-hexadiene. The products isolated from the ozonization of a number of allylic compounds are listed in Table I. It is clear that for substances of types I and II where X = Cl, Br, —OCOCH$_3$ the expected results are obtained, but when X = —OC$_6$H$_4$NO$_2$-*p*, —OH, —OC$_6$H$_5$, —N(C$_2$H$_5$)$_2$ abnormal products are isolated in varying amounts. In general the abnormalities are such as to make the starting materials appear to be mixtures of allylic isomers but as those allylic compounds which are most prone to rearrange give no abnormal products it is quite unlikely that allylic rearrangements of the starting materials before or during ozonization could account for the abnormal results. Direct evidence on this point was obtained by partially ozonizing crotyl alcohol and methylvinylcarbinol. Abnormal products were obtained but the recovered excess alcohols were not detectably isomerized. Furthermore, similar results were obtained by hydrogenation[5] and analysis of the volatile aldehyde mixture as by hydrolysis followed by oxidation and analysis of the volatile acid mixture.

TABLE I

VOLATILE ACIDS FROM THE OZONIZATION OF ALLYLIC COMPOUNDS OF THE TYPE RCH=CH—CHR'X

Compounds	Volatile acids	Found %[a]	Calcd. %
$CH_3CH=CH-CH_2Cl$ $CH_3CHClCH=CH_2$ [b]	Acetic	77	79[c]
	Formic	23	21
$CH_3CH=CHCH_2Br$ $CH_3CHBrCH=CH_2$ [b]	Acetic	82	85[c]
	Formic	18	15
$CH_3CH=CHCH_2OCOCH_3$	Acetic	100	100
$CH_3CH=CHCH_2OC_6H_4NO_2$-*p*	Acetic	92	100
	Formic	8	0
$CH_3CH=CHCH_2OC_6H_5$	Acetic	85	100
	Formic	15	0
$CH_3CH=CHCH_2OH$[d]	Acetic	77	100
	Formic	23	0
$CH_3CHOHCH=CH_2$	Acetic	25	0
	Formic	75	100
$CH_3(CH_2)_3CHOHCH=CH_2$[e]	Formic	62	100
	Valeric	38	0
$CH_3(CH_2)_2CHOHCH=CHCH_3$[f]	Acetic[h]	50	100
	Butyric	50	0
$CH_3CH_2CHOHCH=CHCH_3$[g]	Acetic[h]	85	100
	Propionic	15	0
$C_6H_5CH=CHCH_2OH$	Benzoic	40	100
	Formic	60	0
$CH_3CH=CHCH_2OC_2H_5$	Acetic	75	100
	Formic	25	0
$CH_3CH(OC_2H_5)CH=CH_2$	Acetic	35	0
	Formic	65	100
$CH_3CH=CHCH_2N(C_2H_5)_2$	Acetic	46	100
	Formic	54	0

[a] Values represent the composition of the volatile acid mixtures which were obtained in 30–80% yield. [b] Mixture of allylic isomers was used. [c] Composition estimated from refractive index. [d] Ozonization and hydrogenation gave a 17% yield of formaldehyde. [e] Ozonization and hydrogenation gave a 50% yield of valeraldehyde and 35% of α-hydroxycaproic acid. [f] Ozonization and hydrogenation gave butyraldehyde (35%). [g] Ozonization and hydrogenation gave a 19% yield of acetaldehyde and a 20% yield of formaldehyde. [h] Some formic acid was present and the analytical figures may be somewhat in error.

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[1] Presented in part before the Division of Organic Chemistry at the Buffalo meeting of the American Chemical Society, September, 1942.

[2] (a) Winstein and Young, THIS JOURNAL, **58**, 104 (1936); (b) Young and Lane, *ibid.*, **59**, 2051 (1937); **60**, 847 (1938); (c) Young, Richards and Azorloza, *ibid.*, **61**, 3070 (1939); (d) Roberts, Young and Winstein, *ibid.*, **64**, 2157 (1942); (e) Young and Andrews, *ibid.*, **66**, 421 (1944).

[3] (a) Hurd and Williams, *ibid.*, **58**, 2636 (1936); (b) Hurd and Pollock, *J. Org. Chem.*, **3**, 550 (1939).

[4] Dyer, *J. Biol. Chem.*, **28**, 445 (1917).

[5] Fischer, Düll and Ertel, *Ber.*, **65**, 1467 (1932).

The extent of the abnormal ozonolysis reaction for comparable compounds appears to be related to the basicity of the unshared electron pairs on the atom joining the radical X to the allylic system. For example, with a series of crotyl derivatives when X = Br, Cl or $—OCOCH_3$ no abnormal products were found, while for other radicals an approximate order of degree of abnormality was as follows: $—OC_6H_4NO_2\text{-}p < —OC_6H_5 < —OH < —OC_2H_5 < —N(C_2H_5)_2$. The unshared electrons of the bridge oxygen atom of the acetoxy radical might be expected to be less available than those of an ether linkage by virtue of contributions of resonance forms involving the carbonyl oxygen. Similarly the ether oxygen of *p*-nitrophenyl crotyl ether is expected to be less basic than that of crotyl phenyl ether because of electron withdrawal by resonance contributions of the nitro group. α,β-Unsaturated compounds of the type $CH_3CH{=}CH—COR$ (III) were also found to undergo abnormal ozonolysis to give formic acid and the extent of the abnormality appears to be in the order, R = —OH < —H < $—C_2H_5$. These results are given in Table II.

Table II

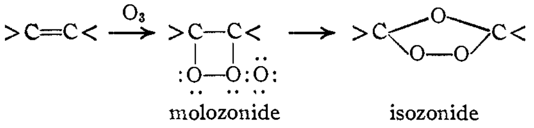
Volatile Acids from the Ozonization of α,β-Unsaturated Carbonyl Compounds of the Type $CH_3CH{=}CHCOR$

R	% CH_3COOH	% HCOOH
—OH	95	5
—H	90	10
$—C_2H_5$[a,b]	29[c]	13

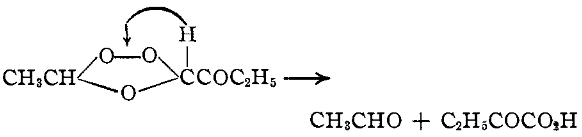
[a] Catalytic hydrogenation was used. [b] A 72% yield of propionic acid was obtained. [c] Isolated as acetaldehyde.

One of the interesting features of the ozonization of the compounds which gave abnormal results was the liberation of considerable quantities of carbon monoxide either spontaneously or on gentle warming. In every case after the evolution of gas was complete the residue gave no test for active peroxide with potassium iodide. For example, the product of the ozonization of 4-hexen-3-one decomposed spontaneously, even in an ice-bath, with the liberation of carbon monoxide and a small amount of carbon dioxide. After the reaction had subsided the ozonide absorbed very little hydrogen on catalytic hydrogenation. Distillation of the reaction products gave yields of 29% of acetaldehyde, 72% of propionic acid and 13% of formic acid. It is significant that neither of the volatile acids is an expected ozonization product.

Mechanism of the Abnormal Ozonization Reaction.—Staudinger[6] has suggested that ozonization of an unsaturated compound proceeds through the following steps

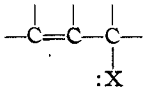


Considerable support for Staudinger's mechanism has been furnished by the investigations of Rieche and others.[7,8,9,10] Fischer, Düll and Ertel[5] have supplemented the Staudinger mechanism with the so-called "acid rearrangement" of isoözonides to account for the production of acids in the decomposition of ozonides. As applied to the ozonide of 4-hexen-3-one this mechanism would be expected to operate as follows



To account for the rapid liberation of carbon monoxide by the spontaneous decomposition of the ozonide it is necessary to assume an unlikely facile decomposition of the α-keto acid occurring along with a simultaneous cleavage reaction to give formic and propionic acids.

A more satisfactory explanation for the abnormal ozonization of certain α,β-unsaturated carbonyl compounds and allylic systems is an extension of the reasoning applied by Staudinger to account for the rearrangement of ozonides to isoözonides. As previously pointed out that as the availability of electrons on group X in



$$—\overset{|}{C}{=}\overset{|}{C}—\underset{\underset{:X}{|}}{\overset{|}{C}}—$$

becomes greater or as X becomes more basic the ratio of abnormal to normal product increases and for this reason it might be expected that an unshared electron pair on X participates in some way in the reaction. We suggest that X may aid the molozonide to rearrange abnormally by donating its electron pair to an oxygen of the molozonide group followed by a rearrangement similar to that postulated for the conversion of a cyclic ketone to a lactone by Caro's acid,[11,12] thus competing with the normal rearrangement which gives the isoozonide of Staudinger.

Similar mechanisms may be proposed for the abnormal ozonization of other allylic systems of types I and II and α,β-unsaturated carbonyl compounds each being featured by the formation of a formic acid derivative which may decompose to give carbon monoxide or be hydrolyzed to the free acid depending on the experimental conditions

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[6] Staudinger, *Ber.*, **58**, 1088 (1925).

[7] Rieche, "Alkylperoxyde und ozonide," T. Steinkopf, Dresden, 1931.

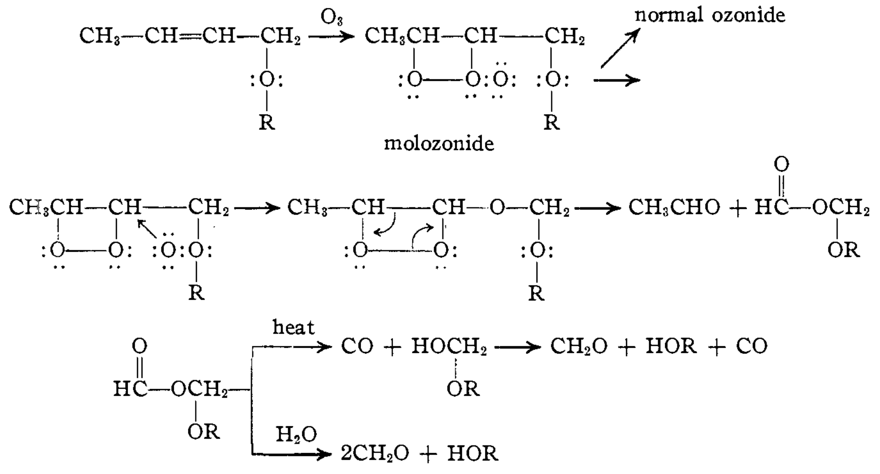
[8] Rieche and Meister, *Ber.*, **65**, 1274 (1932).

[9] Lehmann, Inaugural Dissertation, Leipzig, 1938.

[10] Briner and Schnorf, *Helv. Chim. Acta*, **12**, 154 (1929).

[11] Baeyer and Villiger, *Ber.*, **32**, 3625 (1899); **33**, 858 (1900).

[12] Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1926).



Additional support for the postulated mechanism is afforded by the thermal decomposition of the ozonides from some compounds in which the carbon chain is branched. α-Methyl-β-ethylacrolein gave carbon monoxide, acetic acid and propionaldehyde as predicted. Acetic acid in considerable quantity was isolated from the decomposition of the ozonide of 3,4-dimethyl-3-hexen-2-one although acetic anhydride is the expected reaction product. However, it is not unlikely that sufficient water was present or formed in the reaction mixture to effect hydrolysis of the primary reaction products.

Experimental Part

Source of Compounds Ozonized.—Alkylvinylcarbinols were prepared from acrolein or crotonaldehyde by the method of Delaby[13] as modified by Prevost.[14] Physical properties were determined as follows: methylvinylcarbinol, b. p. 97° n^{25}D 1.4120; propylvinylcarbinol, b. p. 133°, n^{25}D 1.4243; butylvinylcarbinol, b. p. 154–155°, n^{25}D 1.4312; phenylvinylcarbinol, b. p. 100–101° (15 mm.); 4-hexen-3-ol, b. p. 135–136° and 2-hepten-4-ol, b. p. 63.4° (15 mm.).

The **butenyl chloride** mixture was obtained by fractional distillation of a mixture kindly furnished by the Shell Development Company. The **butenyl bromide** equilibirum mixture was prepared by the method of Winstein and Young.[2a] **Crotonic acid** was a recrystallized Eastman Kodak Co. product. **Crotonaldehyde** was kindly furnished by the Niacet Chemicals Company. The procedure described by Adams and Geissman[15] was used for the preparation of 2,4-hexadiene; yield 65%, b. p. 81–82°, n^{20}D 1.4495. **Crotyl acetate** and **α-ethylcrotyl acetate** were made by the reaction of the respective alcohols with acetic anhydride at 120°.

The preparation of 4-hexen-3-one was carried out by a method similar to that of Blaise.[16] A mixture of zinc dust (70 g.), propionitrile (56 g.) and benzene (200 ml.) was heated to refluxing and allyl bromide added slowly over a two-hour period. The mixture was cooled with an ice-bath and water (50 ml.) was added slowly followed by 6 *N* sulfuric acid (200 ml.). The benzene layer was separated and distilled. The fraction boiling between 125–138° was refluxed with 4 *N* sulfuric acid (100 ml.) for thirty minutes. The product was extracted with benzene and the benzene extract was shaken with dilute sodium carbonate solution, then with water, dried and distilled. The yield of 4-hexen-3-one was 21 g.; b. p. 138–139°, n^{20}D 1.4388.

The preparation of α-methyl-β-ethylacrolein, b. p. 134–135°, was accomplished by the aldol condensation and dehydration of propionaldehyde.

Crotyl phenyl ether (b. p. 89° (10 mm.), n^{22}D 1.5195) was supplied by Dr. S. J. Cristol. **Butenyl ethyl ethers** kindly furnished by Dr. S. Winstein had the following properties: crotyl, b. p. 99°, $n^{18.5}$D 1.4048; methlvinylcarbinol $n^{18.8}$D 1.3901.

Crotyl *p*-nitrophenyl ether was prepared by refluxing overnight a mixture of sodium *p*-nitrophenoxide (0.096 mole) in 75 ml. of absolute alcohol with 7.0 g. of crotyl chloride. Water (50 ml.) was added, the product was filtered and crystallized from aqueous methanol. The yield was 9.0 g. (60%); m. p. 78–79°.

Anal. Calcd. for $C_{10}H_{11}O_3N$: C, 62.2; H, 5.74. Found: C, 61.98; H, 6.11.

Ozonization Procedure.—The source of ozone was a machine manufactured by the United States Ozone Company. Tank oxygen dried by passage through a Dry Ice trap was employed. The ozone concentration was usually 2–3%. Wherever the solubility of the compound permitted the ozonization was carried out in a Dry Ice-cooled vessel. Care was taken to prevent over-ozonization by testing for excess unsaturation with bromine in carbon tetrachloride or by stopping the ozonization as soon as a blue color developed at Dry Ice temperatures.

The choice of solvent was governed by the method of decomposing the ozonide. Ethyl acetate was best suited for hydrogenation while chloroform, ligroin, hexane or carbon tetrachloride were used for the hydrolysis and ligroin in the thermal decomposition experiments.

Hydrolysis, Oxidation of Ozonides and Analysis for Acid Products.—The solution of ozonide (from 0.02–0.04 mole of unsaturated compound in 100 ml. of solvent) was added in small portions to 100 ml. of water and allowed to stand until hydrolyzed. Sodium hydroxide and freshly prepared silver oxide were added, using two moles of each compound for each mole of ozonide and the mixture refluxed for three or four hours. The precipitated silver was filtered, the filtrate acidified and distilled to separate the volatile acids which were analyzed by Dyer's method.[4]

Reduction of Ozonides.—For the reductive decomposition experiments of the ozonides the well-known zinc reduction procedure of Whitmore and Church[17] or the hydrogenation method of Fischer and Düll and Ertel[5] was employed. The aldehydes were identified by the usual derivatives. Mixtures of acetaldehyde and formaldehyde were analyzed roughly by the dimethone method[18] and in some cases formaldehyde was estimated separately by reduction of mercuric chloride.

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[13] Delaby, *Compt. rend.*, **175**, 967 (1922).

[14] Prevost, *Ann. chim.*, **10**, 113, 147 (1928).

[15] Adams and Geissman, *ibid.*, **61**, 2083 (1939).

[16] Blaise, *Bull. soc. chim.*, **33**, 39 (1905).

[17] Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932).

[18] Ionescu and Slusanschi, *Bull. soc. chim.*, **53**, 909 (1933).

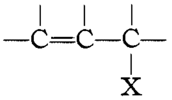
Thermal Decomposition of the Ozonides.—The solution of the ozonide (usually from about 2 g. of unsaturated material) in ligroin was warmed gently in a water-bath until no further reaction occurred. The effluent gases were passed through a Dry Ice trap and collected in a bulb. The gases were analyzed by Mr. Alvin Sellers, using the micro methods developed in the laboratory by Dr. F. E. Blacet, and were found to consist of carbon monoxide mixed with a small amount of carbon dioxide. Depending on the extent of abnormal ozonization, from 0–32% of the theoretical quantity of carbon monoxide was liberated. In those experiments where abnormal ozonization was the predominant reaction the residue from the thermal reaction gave no test for active ozonide with potassium iodide.

Summary

1. Abnormal products have been isolated from the ozonization of allylic isomers of the types R—CH═CH—CHR′X and RCHX—CH═CH-R′. The abnormalities were often such as to make the starting materials appear to be mixtures of allylic isomers. Carbon monoxide is liberated spontaneously or on gentle warming of abnormal ozonides.

2. Certain α,β-unsaturated carbonyl compounds also gave abnormal ozonization products.

3. For a series of compounds of the type



$-\overset{|}{C}=\overset{|}{C}-\underset{X}{\overset{|}{\underset{|}{C}}}-$

the extent of abnormal reaction appears to be related to the basicity of unshared electron pairs carried by group X. On this basis a mechanism for the abnormal reaction has been suggested involving the participation of group X in a rearrangement of the molozonide.

LOS ANGELES 24, CALIFORNIA

RECEIVED SEPTEMBER 27, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Diffraction of X-Rays by Aqueous Solutions of Hexanolamine Oleate

BY SYDNEY ROSS* AND J. W. MCBAIN

A number of papers published in Germany since 1937[1] have reported results on the diffraction of X-rays by soap solutions. The importance of these researches, in establishing the presence of lamellar micelles in aqueous soap solutions as well as in elucidating some of the mechanism of "solubilization,"[2] requires that independent confirmation and further investigation be forthcoming.

This paper presents results on a series of clear transparent aqueous systems of hexanolamine oleate at room temperature, ranging in concentration from 25 to 92% by weight of soap, a wider concentration range than any previously reported in detail. The most concentrated and the most dilute systems were fluid isotropic solutions. All others were anisotropic liquids ranging in consistency from oil to grease. X-Ray data are already available on the anhydrous crystalline material.[3] The X-ray diagrams obtained from these colloidal solutions differ from most photographs of liquids in that the inner spacing and its orders are sharp and definite and so render the reported measurement of more than customary accuracy.

Experimental

Materials and Methods

The hexanolamine oleate used is the same as that previously reported.[3] The series of aqueous systems was made by successive additions of conductivity water and prolonged stirring. The concentration in each case was obtained by weighing and is reported as weight per cent.

The source of X-rays was a General Electric beryllium window tube, with a copper target and nickel filter. The X-ray unit was the General Electric XRD 2.

The liquid was held in a stainless steel cell that had two thin mica windows. It was found that "Cenco Varniton" is useful in attaching the mica windows to the metal as, when dried, it is not affected by these solutions. The two halves of the cell were held together by pressure, with a thin film of Dow Corning stopcock grease between them. No leaking of liquid or evaporation of the solvent took place during the exposure time (six hours) when the cell was carefully put together.

The calibration of the sample-to-plate distance (50.0 mm.) was checked by using solid hexanolamine oleate. Once established it was not altered throughout the course of the experiments. It was checked at various times and found to remain constant.

Microphotometer records of each diffraction diagram were obtained, using the recording microphotometer designed by Leighton, Smith and Henson.[4] Care had to be taken in every case to obtain a diameter across the film that avoided spots arising from the mica windows.

Results

In the more concentrated systems (above 40% hexanolamine oleate) the water halos do not appear. A halo that appears at all concentrations is observed at d = 4.5 to 4.6 Å., calculated from the Bragg formula. This halo corresponds in position to that portion of the diagram of the crystalline soap where the most intense side-spacings occur, more especially that provisionally

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[1] (a) K. Hess and J. Gundermann, *Ber.*, **70**, 1800 (1937); (b) W. Philippoff and K. Hess, *ibid.*, **70**, 1808 (1937); (c) K. Hess, H. Kiessig and W. Philippoff, *Naturwissenschaften*, **26**, 184 (1938); (d) H. Kiessig and W. Philippoff, *ibid.*, **27**, 593 (1939); (e) K. Hess, W. Philippoff and H. Kiessig, *Kolloid-Z.*, **88**, 40 (1939); (f) J. Stauff, *ibid.*, **89**, 224 (1939); (g) H. Kiessig, *ibid.*, **96**, 252 (1941); (h) W. Philippoff, *ibid.*, **96**, 255 (1941); (i) K. Hess, *Fette u. Seifen*, **49**, 81 (1942); (j) H. Kiessig, *Kolloid-Z.*, **98**, 213 (1942).

[2] J. W. McBain, "Advances in Colloid Science," Vol. 1, New York, 1942, pp. 99–142.

[3] S. Ross and J. W. McBain, THIS JOURNAL, in press.

[4] P. A. Leighton, F. Smith and F. C. Henson, *Rev. Sci. Instruments*, **5**, 431 (1934).