

Oxidation as an Aid in the Identification of Unsaturated Hydrocarbons by Gas Chromatography

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Ozone oxidation is shown to be a useful analytical tool for the identification of unsaturated hydrocarbons condensed from analytical gas chromatographs. Several of the products formed on oxidation were determined quantitatively and thus information was obtained about the position and number of various unsaturated bonds in the molecule. The qualitative analysis of the oxidation products was based on the paper chromatographic separation of the dinitrophenylhydrazones prepared from the carbonyl compounds formed on oxidation.

To aid in the identification of unsaturated hydrocarbons separated by gas chromatography, various methods are being studied in this laboratory. Recently¹, a report was published on hydrogenation methods developed for this purpose and in the present paper the utilization of ozone oxidation is described.

Among oxidation methods used in the structural investigation of unsaturated hydrocarbons, ozonolysis has generally been regarded as the best method² since a shift in the position of the unsaturated bonds or other rearrangements are not likely to take place (*cf.*, however, below).

Our principal aim was to determine, quantitatively, unsaturated bonds in 1- and 2-position, *i.e.* >C=CH_2 , >C=CH-CH_3 , $\text{-C}\equiv\text{C-CH}_3$ and $\text{>C=C(CH}_3)_2$, and further to prove the presence of alkadienes with cumulated and conjugated double bonds. The analysis was based on a quantitative determination of the following ozonolysis products: formaldehyde, acetaldehyde, acetone, glyoxal and carbon dioxide. It was also desired to obtain qualitative analysis of the carbonyl compounds formed on oxidation.

The oxidative cleavage of the unsaturated bonds was found to proceed regularly³ except in the case of 1,2-alkadienes. According to Bon⁴ this reaction can be written



Table 1. Oxidation of unsaturated hydrocarbons by ozone.

Hydrocarbon oxidized	Amount	Oxidation products, mmole (yield %)				
		Name	mmole	Formaldehyde	Acetaldehyde	Acetone
1-Heptene	0.052		0.050 (96)			
1-Octene	0.095		0.092 (97)			
1-Nonene	0.061		0.064 (105)			
1-Undecene	0.073		0.073 (100)			
2,3,3-Trimethyl-1-butene *	0.108		0.077 (71)			
2,4,4-Trimethyl-1-pentene	0.070		0.060 (86)			
1,5-Hexadiene	0.107		0.206 (96)			
<i>Trans</i> -1,3,5-hexatriene **	0.024		0.042 (88)			
Styrene	0.131		0.127 (97)			
<i>Trans</i> -2-octene	0.027			0.025 (93)		
<i>Trans</i> -2- <i>trans</i> -4-hexadiene **	0.030			0.068 (113)		
1,2-Pentadiene	0.152	0.060 (40)	0.048 (32)		0.083 (55)	
1,2-Hexadiene	0.104	0.052 (50)	0.042 (40)		0.047 (45)	
1,2-Heptadiene	0.152	0.080 (53)	0.060 (39)		0.064 (42)	
2-Pentyne	0.159		0.129 (81)			
2,4,4-Trimethyl-2-pentene	0.025				0.022 (88)	

* Criegee * has reported that certain olefins of this type ($R_2C=CH_2$) are oxidized by ozone to aldehydes $R_2CH-CHO$ and carboxylic acids $R_2CH-COOH$.

** The yield of glyoxal was not quantitative.

In the ozonolysis of the three 1,2-alkadienes in Table 1, however, acetaldehyde was unexpectedly formed. This fact seems to imply that a rearrangement occurs during the oxidation. The results are consistent with an isomerization to a 2-alkyne *:



According to the formulas given above, the sum of formaldehyde and acetaldehyde or carbon dioxide and acetaldehyde should equal 100 %. This was in fact found to be the case within the limits of error valid for our experiments (*cf.* Table 1). The formation of carbon dioxide is indicative of the presence of an allene. Alkadienes with conjugated double bonds give rise to glyoxal. The yield obtained was, however, rather variable and generally considerably less than expected. Because of this, a quantitative analysis could not be based on the glyoxal determination.

In most cases the yield of oxidation products was over 80 %. This result must be considered satisfactory in view of the losses encountered in the chromatographic separation and during the oxidation procedure. It is seen from Table 1 that the presence of several unsaturated bonds in a molecule, *e.g.* in 1,5- and 2,4-hexadiene and in 1,3,5-hexatriene, is clearly revealed by the amount of formaldehyde and acetaldehyde formed.

* The ready isomerization of allene to methylacetylene is a well-known reaction ⁵.

To map out the products formed during the ozone oxidation and prior to their quantitative determination a paper chromatographic separation of the dinitrophenylhydrazones formed on reaction of the ozonized solution with 2,4-dinitrophenylhydrazine was made⁶. A measure of the amount of a dinitrophenylhydrazone contained in a spot on the filter paper was obtained by cutting out the spot, extracting the paper with pyridine and titrating the pyridine solution according to Sensabaugh *et al.*⁷ using 0.01 N tetrabutylammonium hydroxide. This titration method was found to be useful for determining whether a spot on the filter paper was formed from a major or a minor product in a hydrocarbon mixture. It was also usable for tracing bis-hydrazones formed from difunctional carbonyl compounds since two inflexion points were obtained in the titration curve in this case. It should be emphasized that this titration method does not give an accurate measure of the carbonyl compounds formed in the ozonolysis, since, in the method used, the conversion of the carbonyl compounds into their dinitrophenylhydrazones was not quantitative.

The paper chromatographic method was not too selective, merely giving the carbon number for monofunctional carbonyl compounds up to about C₇. Because of their low R_F -values, the dinitrophenylhydrazones of low molecular difunctional carbonyl compounds, *e.g.* glyoxal and methylglyoxal, could be distinguished from the dinitrophenylhydrazones of monofunctional carbonyl compounds.

The present investigation has proved the utility of ozone oxidation for the identification of unsaturated hydrocarbons separated by gas chromatography. The method, however, is not ideal in all respects. For the qualitative identification of the oxidation products, a more selective and more rapid method than the paper chromatographic one used would be desirable. Furthermore, the quantitative determination is somewhat laborious and only applicable to certain of the oxidation products. The results of the quantitative determinations are collected in Table 1.

It would be a great advantage if the analysis of the oxidation mixture could be made by gas chromatography. We think that the problem could be successfully attacked by utilizing a flame ionisation detector and by performing the ozonolysis in a solvent for which the detector in question is blind.

EXPERIMENTAL

Condensation of fractions from the chromatograph. A known volume of a hydrocarbon fraction was injected into the chromatograph by means of a Hamilton syringe and, after separation, appropriate pure compounds were condensed in a sample tube immersed in a dry ice-acetone bath. The amount of material in the condensed fractions was calculated on the basis of the chromatogram, putting area percentage equal to weight percentage.

Ozonolysis. Among the limited number of usable solvents, ethyl acetate was chosen. When pure, it was not attacked by ozone. It was not necessary to take any special measures in order to decompose the ozonides; the oxidized solution could be treated directly by the various reagents used to determine the carbonyl compounds quantitatively or to transform them into dinitrophenylhydrazones.

Ethyl acetate (0.5 ml) was filled into the sample tube and the level of the solvent marked on the tube. A wash-bottle containing a solution of barium hydroxide (for the absorption of carbon dioxide, *cf.* below) was coupled to the sample tube and the train

was concluded by another wash-bottle with an acidified potassium iodide solution to indicate any break-through of ozone. The sample tube was cooled to 0° in iced water and the reaction train connected to the ozone generator and a stream of 10 ml of oxygen per min. bubbled through until the uptake of ozone was complete as shown by the indicator wash-bottle*.

Ethyl acetate was added to the cool-finger to compensate for losses during the oxidation procedure. Of the contents of the sample tube, 0.1–0.2 ml was used for the preparation of dinitrophenylhydrazones. The remainder was used for the quantitative determination of one or several of the following compounds: formaldehyde, acetaldehyde, acetone and glyoxal. As the quality of commercial ethyl acetate, also of analytically pure samples, was rather variable, it was necessary to oxidize a sample and investigate the oxidation products by paper chromatography before using it as solvent in an experiment. Any carbon dioxide formed during the ozonolysis was determined in the barium hydroxide solution as detailed below.

Preparation and paper chromatographic separation of dinitrophenylhydrazones. To the solution of ozonides in ethyl acetate was added 1 ml of a dinitrophenylhydrazine reagent made up by dissolving 1 g of 2,4-dinitrophenylhydrazine in 25 ml of 85 % phosphoric acid using a steam bath and, after cooling, diluting the mixture to 50 ml with ethanol⁸. The reaction mixture was heated for some minutes in a water bath (60°) and after cooling allowed to stand for 30 min. The dinitrophenylhydrazones formed were extracted 5 times by 0.5 ml portions of pentane. The pentane was evaporated and the residue dissolved in 0.1 ml pentane. This solution was analyzed by paper chromatography according to Meigh⁶ using heptane-methanol, the heptane phase being the mobile one.

Quantitative determinations

Formaldehyde. For the quantitative determination of formaldehyde, the chromotropic acid method was used⁹⁻¹¹. The density of the red solution formed was measured at 570 $m\mu$ against a blank of ethyl acetate treated in the same way as the sample. The amount of formaldehyde in the sample was read from a standard curve prepared by subjecting known amounts of formaldehyde in ethyl acetate, determined by titration¹², to the method.

Acetaldehyde and acetone have been shown to interfere with the determination of formaldehyde by the present method¹¹. We have, in accordance with the recommendations of Bricker and Johnson¹¹, reduced this interference by using larger amounts than usual of chromotropic acid and by dilution with sulphuric acid instead of water.

Acetaldehyde. Eegriive¹³ has proposed a colorimetric method for the quantitative determination of acetaldehyde which was found applicable in this case. The procedure developed by Tompsett¹⁴ was used here. It involves a reaction with *p*-hydroxydiphenyl in the presence of copper sulphate and conc. sulphuric acid. A red colour is developed and the density of the solution was measured at 560 $m\mu$ against a blank of ethyl acetate treated in the same way as the sample. The amount of acetaldehyde was determined from a calibration curve. We have investigated the influence of a number of lower aldehydes and ketones on the results but have not found any appreciable effect**.

Acetone. For the quantitative determination of acetone, a colorimetric method has been worked out by Ravin¹⁵. It is based on the reaction of acetone with salicylaldehyde in the presence of strong alkali and heat giving red dihydroxybenzalacetone. The original method was later on modified by Nadeau¹⁶ and Pawan¹⁷. The density of the solution was measured at 520 $m\mu$ against a blank of ethyl acetate treated like the sample. The amount of acetone was obtained from a calibration curve.

Glyoxal. For the quantitative determination of glyoxal, a method devised by Wise *et al.*¹⁸, using dianilinoethane, was employed. The density of the coloured solution formed

* The ozone contents of the oxygen was generally about 5 %.

** Formaldehyde was stated by Tompsett¹⁴ to interfere with the determination of acetaldehyde and he has described an aeration procedure for the separation of these aldehydes prior to the determination of acetaldehyde. Because of the relatively large errors, inherent in our experiments, we have, however, not found it necessary to make any separation.

was measured at 550 μ . As usual, ethyl acetate treated just like the sample was used in the reference beam and the amount of glyoxal read from a calibration curve. Methylglyoxal was found to interfere with the determination of glyoxal.

Carbon dioxide. Carbon dioxide formed upon the ozonolysis of 1,2-alkadienes was determined by absorbing it in a barium hydroxide solution in a wash-bottle placed after the sample tube in the oxidation train and titrating the excess of base using 0.01 N hydrochloric acid and phenolphthaleine as indicator¹⁹. A blank was prepared in the same way, using pure ethyl acetate in the sample tube.

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