

Ozonolysis of Some Monosubstituted Maleic Acids

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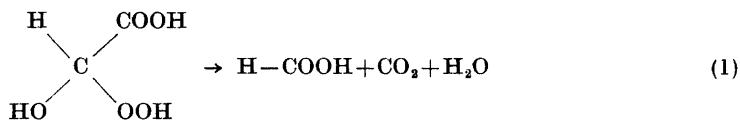
Citraconic, chloromaleic, phenylmaleic, and hydroxymaleic acids and their sodium salts have been ozonised in aqueous solution. Reaction paths are discussed and mechanisms suggested for the formation of some unexpected products.

The effect of substituents on the direction of ozonolytic cleavage in unsymmetric olefins has been a matter of interest for some time.^{1,2}

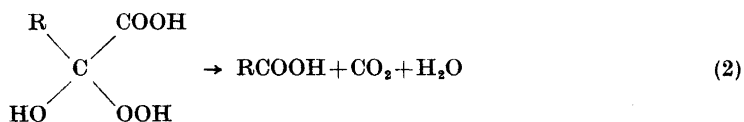
In the present investigation citraconic, phenylmaleic, chloromaleic, and hydroxymaleic acids as well as their disodium salts have been ozonised in aqueous solution.

The analytical results are summarised in Tables 1-5.

Earlier works^{3,4} have established that pyruvic acid is a product from the ozonolysis of citraconic acid. The present results are best explained by an anomalous ozonolysis with a rearrangement at the hydroperoxy stage.



The carbonyl fragment in this process is pyruvic acid.



In this case the carbonyl fragment is glyoxylic acid.

Within the limits of analytical error the stoichiometric requirements of reactions (1) and (2), (R = CH₃) are supported by Table 1.

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Table 1. Analytical results from the ozonolysis of 10 mmoles of citraconic acid.

	Total acid (mequiv.)	Sum pyruvic and glyoxylic acid (mmole)	Pyruvic acid (mmole)	Formic acid (mmole)	Acetic acid (mmole)	Carbon dioxide (mmole)
Free acid	19.9	9.8	1.3	1.2	8.6	9.8
Disodium salt	19.9	9.8	6.6	6.3	3.4	9.9

Table 2. Analytical results from the ozonolysis of chloromaleic acid.

	Ozone absorbed (mmole)	Increase in total acid (mequiv.)	Oxalic acid (mmole)	Glyoxylic acid (mmole)	Chlorine (mmole)	Carbon dioxide (mmole)
Free acid	6.5	4.5	2.2	4.1	6.3	10.2
Disodium salt	6.8	0.0	0.0	6.6	6.7	12.4

Table 3. Analytical results from the ozonolysis of phenylmaleic acid.

	Ozone absorbed (mmole)	Glyoxylic acid (mmole)	Phenyl-glyoxylic acid (mmole)	Benzoic acid (mmole)	Formic acid (mmole)	Carbon dioxide (mmole)
Free acid	9.7	8.0	1.5	7.5	1.4	9.5
Disodium salt	10	4.2				

Table 4. Analytical results from the ozonolysis of hydroxymaleic acid in aqueous solution.

Ozone absorbed (mmole)	Total acid (mequiv.)	Oxalic acid (mmole)	Formic acid (mmole)	Mesoxalic acid (mmole)	Carbon dioxide (mmole)
9.6	21.9	3.9	3.9	5.1	9.2

Table 5. Analytical results from the ozonolysis of hydroxymaleic acid in basic solution.

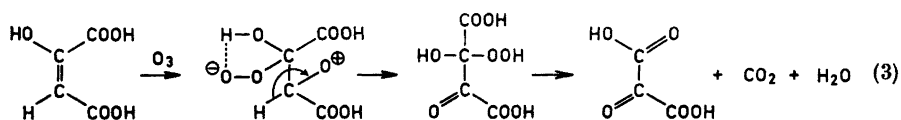
Ozone absorbed (mmole)	Total acid (mequiv.)	Glyoxal (mmole)	Oxalic acid (mmole)	Tartronic acid (mmole)	Oxygen (mmole)	Carbon dioxide (mmole)
9.9	20.0	[0.8]	4.0	6.0	3.4	10.9

Interaction between the hydroperoxides and the carbonyl fragments with formation of peroxidic acetals is considered not to take place to a significant degree, since no peroxides were present after ozonisation.

Chloromaleic acid absorbed ozone much slower than did citraconic acid. The analytical data are therefore based on the amount of absorbed ozone. Also in this case anomalous ozonolysis with rearrangement of hydroperoxides is probably operative; eqns. (1) and (2); R = Cl. The products in Table 2 are the expected ones, and the amounts meet the stoichiometric requirements of the equations.

Phenylmaleic acid absorbed ozone slowly, but excessive frothing during the runs made comparison with the other compounds difficult. Also this acid yielded the products expected from an anomalous ozonolysis through the processes (1) and (2), R = C₆H₅, and in roughly the right amounts (Table 3).

Hydroxymaleic acid absorbed ozone readily, but the products in Table 4 are only in part those expected on the basis of anomalous ozonolysis. Glyoxylic acid is missing, and mesoxalic acid appears in the reaction mixture. Two mechanistic problems are thus posed. The first is solved by the non-participation of reaction (2), R = OH, where glyoxylic acid is the carbonyl partner. The second involves the formation of a C₃-fragment, mesoxalic acid. It is highly suggestive that the hydroxyl group plays a decisive role in this mechanism (3) through hydrogen-bond formation in the primary zwitterion with a certain attenuation of the negative charge which may lead to a C-H rupture preferentially to a C-C bond cleavage:

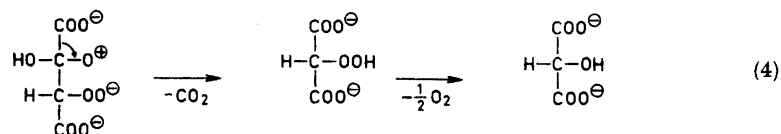


The new hydroperoxidic entity rearranges easily, and with loss of carbon dioxide and water forms mesoxalic acid. The analytical results in Table 4 can be explained by combination of reaction paths (1) and (3).

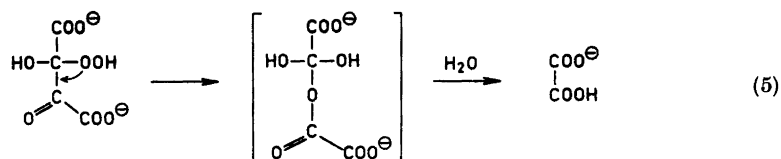
The ozonolysis of the disodium salts of citraconic, chloromaleic, and phenylmaleic acids did not give any new reaction products. However, some of the products from phenylmaleic acid could not be determined. As for the free acids the analytical results can be explained through reaction paths including (1) and (2).

In the case of hydroxymaleic acid the results from the salts are different, as formic and mesoxalic acids have disappeared while glyoxal and tartronic acid are found in the reaction mixture.

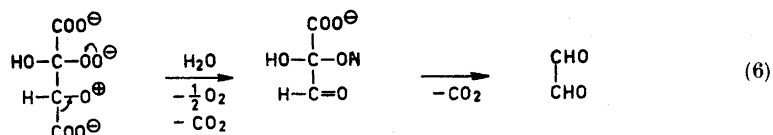
The most likely mechanism for tartronic acid formation is through decarboxylation of the primary zwitterion to the dianion of hydroperoxymalonic acid⁵ which loses oxygen in the alkaline solution (reaction (4)).



Oxalic acid is not formed through reaction (1), where it would occur as the carbonyl partner (R=OH), since formic acid is not found in the reaction mixture. Rearrangement of the hydroperoxide entity in (3) with rupture of the central C—C bond gives two molecules of oxalic acid.



The formation of glyoxal requires loss of oxygen as well as carbon dioxide from the primary zwitterion.



The intermediate mesoxalic semialdehyde anion is decarboxylated in the second step to glyoxal.

From the above results it can be deduced that formation of the Criegee zwitterion during ozonolysis of the free acids mainly occurs at the substituted carbon atom, while the salts give a more random distribution. The results are collected in Table 6, but it is felt, due to the relative scarcity of the material, that further mechanistic inferences are not warranted.

EXPERIMENTAL

Ozonisation technique. Ozonated oxygen was passed through a solution of 10.00 moles of acid in 100.0 ml distilled water. The disodium salts of the acids were prepared by titration with 0.100 N sodium hydroxide. At an oxygen rate of 30 l h⁻¹ the generator produced 2.1–2.6 g O₃ per h. During each run the ozone output was nearly constant. The duration of ozonisation was determined from the absorption curve which was recorded in each case. Reaction temperature was 20–22°C.

Table 6. Zwitterion formation at the substituted carbon atom.

Substituent	Zwitterion in % at substituted C	
	Free acids	Disodium salts
Methyl	87	34
Chlorine	65	100
Phenyl	82	42
Hydroxyl	59	39

Analysis of volatile acids. Formic, acetic, pyruvic, and benzoic acids occurred after ozonolysis in dilute aqueous solution. By the distillation method of Virtanen and Pulkki⁶ formic and acetic acids could be determined as well as mixtures of pyruvic with formic and acetic acids and benzoic with formic acid.

Citraconic acid. The acid employed had m.p. 91.5°C, and its purity was checked by titration.

Pyruvic acid in the ozonised solution was reacted with sodium hypiodite and determined gravimetrically as iodoform. As the reaction is not quantitative, a standard curve had to be worked out.

The sum of carbonyl compounds was determined by precipitating the dinitrophenylhydrazones and correcting for the solubility.

Carbon dioxide was determined by absorption on sodium asbestos. The gas from the reaction vessel was led through acidified potassium iodide, concentrated sulphuric acid and magnesium perchlorate before entering the absorption tube.

The results in Table 1 are means of 8 independent ozonolyses in the case of the free acid and of 5 runs in the case of the disodium salt.

Chloromaleic acid. A commercial sample of chloromaleic anhydride was purified by distillation *in vacuo* and the appropriate amount was dissolved in water before each experiment. Complete hydrolysis was checked by titration.

In order to avoid secondary oxidations of reaction products the reaction was only run until 6.5–6.8 mmoles had been absorbed per 10 mmoles of acid (except in the determination of formic acid where chloromaleic acid would interfere).

Glyoxylic acid was determined by precipitating the dinitrophenylhydrazone and correcting for the solubility.

Oxalic acid was determined as calcium oxalate monohydrate.

Hydrochloric acid was determined as silver chloride.

The results in Table 2 are mean values from 6 ozonolyses for the acid as well as the salt. Formic acid values are means of 3 runs in both cases.

Phenylmaleic acid. The anhydride was prepared and purified in the laboratory. M.p. 119–120°C. Before ozonolysis a sample of the anhydride was treated with cold water for several days, filtered, and the content of acid determined by titration. The titration value was checked after an additional couple of days.

Glyoxylic and phenylglyoxylic acids were precipitated as dinitrophenylhydrazones. These hydrazones were separated by TLC on silica-gel (CCl₄:CH₃COOH, 100:15) and glyoxylic dinitrophenylhydrazone determined spectroscopically.

Benzoic acid precipitated during ozonolysis. The reaction mixture was brought to 200.0 ml and after standing benzoic acid was filtered, dried cautiously and weighed. A correction for the solubility of benzoic acid was applied. The values from this determination are considered less accurate.

Hydroxymaleic acid. The acid was a commercial sample with m.p. 150–152°C.

Mesoxalic acid was precipitated as the calcium salt (together with calcium oxalate). From a solution of the salts in dilute hydrochloric acid a dinitrophenylhydrazone was prepared. This could be shown to be identical with an authentic sample of mesoxalic dinitrophenylhydrazone through its melting point, *R_F*-values in TLC and its UV-

spectrum. Further the elemental analysis and equivalent weight were correct. As an additional proof, the methyl esters of the acidic ozonolysis products were prepared and dimethyl mesoxalate identified in this mixture by GLC.

Quantitatively mesoxalic acid was determined through the dinitrophenylhydrazone according to Clift and Cook.⁷

Hydroxymaleic acid disodium salt. Aqueous solutions of the salt were made from the acid by titration with sodium hydroxide.

Glyoxal was identified through the bis-dinitrophenylhydrazone by TLC and melting point. The quantitative determination of glyoxal was only approximate due to the tendency to polymerisation and based on precipitation of the bisdinitrophenylhydrazone.

Glycolic acid was isolated by evaporating the reaction mixture to dryness and extract the salts with acetone containing a few drops of hydrochloric acid. The acid was at first a syrup which could be brought to crystallisation. M.p. 76–78°C. The IR-spectrum of the acid was identical with that of an authentic sample. After 4 days at 100°C the acid was converted to a substance with m.p. 130°C, no depression with glycolic acid "anhydride".

Tartronic acid. After ozonisation the solution was nearly neutral, but after concentration to a small volume *in vacuo* at 60°C a strong basic reaction developed. On addition of hydrochloric acid copious amounts of carbon dioxide evolved. Evidently a decarboxylation had taken place during the evaporation. By TLC it was shown that the solution contained only glycolic and oxalic acids. Tartronic acid is the only possible substance which can decarboxylate to glycolic acid under the abovementioned conditions. Further evidence for the presence of tartronic acid came from oxidation of the ozonised solution with hydrogen peroxide in presence of ferrous ions. By this reaction mesoxalic acid was produced and identified as the dinitrophenylhydrazone.

Quantitatively tartronic acid was determined as the difference between the total acid content and oxalic acid.

Ozonolysis in the presence of perchloric acid. The four monosubstituted maleic acids were also ozonised in aqueous solution with addition of perchloric acid in order to suppress the ionisation of the acids. The analytical results differed only slightly from those obtained with the pure aqueous organic acids.

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