

Ozonolysis of Maleic Acid in the System Formic Acid - Water

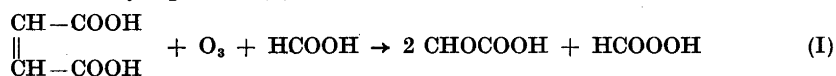
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Maleic acid has been ozonised in formic acid of various concentrations. The yields of active oxygen, "peracid" activity, and glyoxylic acid have been determined. The results are being explained on the basis of different reaction paths. Under suitable conditions the yield of glyoxylic acid approaches 100 %. Some ozonisations were also performed with fumaric acid.

Maleic acid was first ozonised by Harries.¹ He treated an aqueous solution with ozone and found glyoxylic acid as a reaction product, but could detect no oxalic acid. Dorland and Hibbert² ozonised maleic acid in formic acid and reported a yield of 96 % glyoxylic acid and no oxalic acid. In ethyl acetate on the other hand, they found only 14.5 % glyoxylic acid but 80 % oxalic acid. More systematic investigations were made by Briner and Frank³ who performed the ozonisations in water, glacial acetic acid and methanol. In addition sodium maleate (and fumarate) was ozonised in aqueous solution. Ozonisation of maleic acid in water gave glyoxylic, oxalic, and formic acids as well as carbon dioxide in varying proportions depending upon the amount of ozone applied. In glacial acetic acid glyoxylic and formic acids and carbon dioxide were formed, while the reaction in methanol (at -60°C) yielded a product which they believed to be an ozonide. This substance could be decomposed in boiling acetic acid and afforded then glyoxylic and oxalic acids and carbon dioxide. Sodium maleate gave the same products as the free acid although in different proportions.

The present work concerns the "solvolytic ozonolysis" of maleic acid in formic acid of various concentrations. Some aspects of this reaction type have already been reported.⁴⁻⁶ Ideally a solvolytic ozonolysis of maleic acid can be represented by equation (I):



There will, however, be some complicating factors in this picture. Firstly the reaction may take a different course at an intermediate (*e.g.* zwitterion) stage whereby the molecule can be split up into C_1 -fragments or transformed to oxalic acid. Secondly performic acid will vigorously attack glyoxylic acid and can thus reduce the yield with as much as one half. When water in appreciable amounts is present a decrease in peracid formation is to be expected, *e.g.* due to the formation of hydrogen peroxide.

Maleic acid in aqueous solution did not absorb ozone quantitatively. About five moles had to be applied before the acid had reacted completely. This is in agreement with the findings of Noller *et al.*⁷ on the ozonisation rate of maleic acid in acetic acid. The reaction also in this medium was rather slow, but in accordance with the electrophilic nature of ozone, electron-donating groups, *e.g.* methyl, in the neighbourhood of the double bond enhanced the reactivity. The reduced reactivity of the double bond in maleic acid is clearly due to the electron-withdrawing action of the two carboxylic groups.

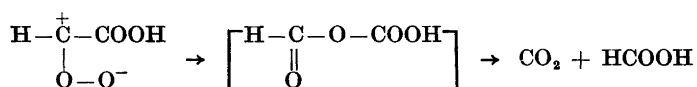
After the ozonisation in water the solution contained only 0.06 g atom active oxygen per mole of starting material, probably exclusively in the form of hydrogen peroxide. Analytical data for other reaction products are collected in Table 1.

Table 1. Products from ozonolysis of maleic acid in water.

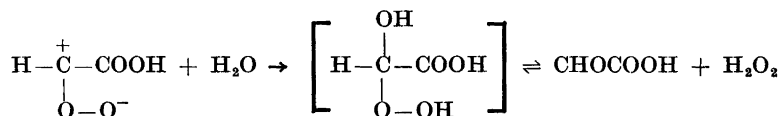
Products	Moles formed per mole starting material	% Recovered carbon
Carbon dioxide	0.76	18.9
Formic acid	1.02	25.6
Glyoxylic acid	1.02	50.9

It is evident that maleic acid is split up into one molecule each of carbon dioxide, formic acid and glyoxylic acid. The deficiency in carbon dioxide must in part be due to difficulties in the analytical procedure.

The reaction path, which is responsible for this result, is very likely a direct rearrangement and decarboxylation of the zwitterion (*i.e.* anomalous ozonolysis):



To a minor extent the zwitterion has reacted with water to give a hydroxyhydroperoxide, which, in analogy to known reactions, can break down into glyoxylic acid and hydrogen peroxide:



Besides being in equilibrium with hydrogen peroxide and glyoxylic acid the hydroperoxide probably breaks down into carbon dioxide, water and formic acid. This reaction is equivalent to a secondary oxidation of glyoxylic acid by hydrogen peroxide.

When maleic acid was ozonised in formic acid of different concentrations, the uptake of ozone was even slower than in water and the reaction time had to be increased by about 50 %. This may be due to a decreased reactivity of maleic acid in the acid milieu, but preliminary experiments showed also that a large part of the ozone was decomposed by passage through formic acid.

The analytical data from the ozonisations in formic acid are collected in Table 2.

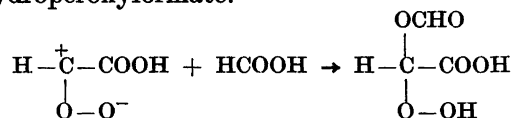
Table 2.

% Formic acid	Total active oxygen % of theoretical	"Peracid", % of theoretical	Glyoxylic acid, % of theoretical
10	13.6	—	53.9
20	15.7	—	56.2
40	28.1	—	63.6
60	32.0	—	68.0
80	39.5	26.5	70.6
90	45.9	37.3	75.7
98—100	59.7	57.8	79.1

After the ozonisation, which had been performed at 3—4°C, dissolved ozone was removed by sweeping the reaction mixture with oxygen for 10 min. At that point total active oxygen and "peracid" were determined iodometrically, while glyoxylic acid was precipitated as a dinitrophenylhydrazone.

Table 2 shows that, as the concentration of formic acid increases, the amount of all determined quantities also increases. "Peracid" determination first becomes unambiguous in 80 % formic acid. In no case was it possible to isolate any performic acid by distillation. The "peracid" part of the active oxygen also increases rapidly, so that in concentrated formic acid virtually all activity seems to stem from "peracid". The remainder is for the greater part probably hydrogen peroxide.

From these results it is conceivable that at lower concentrations of formic acid the direct decarboxylation of the zwitterion is the dominant reaction. Some hydration of the zwitterion is also likely to occur. As the concentration of formic acid is increased, another reaction is bound to take place *viz.* the formation of a hydroperoxyformate:



This type of reaction is known to occur in the ozonolysis of octahydro-naphthalene in acetic acid solution.⁸ The fact that no performic acid could be found on distillation strongly indicates that peracid formation plays no

significant part in the ozonolysis reaction under study. It is likely that the "peracid", which could be titrated with the standard titration method, in fact was the above-mentioned hydroperoxyformate. This entity must be very reactive towards reducing agents, but not quite as reactive as a peracid since the "peracid" titration only became clear-cut at high concentrations of formic acid.

The ten-fold increase in active oxygen when going from water to concentrated formic acid can be ascribed to the relative reaction rates of the two solvent molecules with the zwitterion as well as to the relative stabilities of the hydroperoxides.

The reaction schemes, which have been considered above, imply a strict relationship between the amounts of active oxygen and glyoxylic acid. If there is a 100 % yield of active oxygen, there should have been no decomposition of zwitterion or hydroperoxide or oxidation of glyoxylic acid, which therefore also must appear in 100 % yield. On the other hand, if the content of active oxygen is nil, one half of the glyoxylic acid must have been oxidised and the yield of this product has decreased to 50 %. Between these extremes a linear relation should exist. Taking the yields of glyoxylic acid from Table 2 and calculating the expected amounts of active oxygen we get the figures of Table 3 which are compared with the found values.

Table 3.

% Formic acid	Act. oxygen, % calculated	Act. oxygen, % found
10	7.8	13.6
20	12.4	15.7
40	27.2	28.1
60	36.0	32.0
80	41.2	39.5
90	51.4	45.9
98-100	58.2	59.7

The agreement between calculated and found values must be considered as good, especially when taking into consideration the numerous complications which are apt to emerge in ozonolytic processes. This agreement also lends support to the correctness of the overall picture drawn of the ozonolysis of maleic acid.

Measurements on the disappearance of active oxygen in the reaction mixture after termination of the ozonolysis show that after about four hours only 10 % of the active oxygen is left. When the oxygen activity is zero there would be expected to remain glyoxylic acid in an amount of 50 % of theoretical. Analyses show that this is very nearly the case when 10 % formic acid is used as solvent, but the amount increases gradually so that in concentrated formic acid there is 59 % glyoxylic acid left when the active oxygen has disappeared. Evidently there must occur side-reactions where oxygen activity is consumed but not glyoxylic acid. One possibility is the elimination of molecular oxygen.

So far the best yield of glyoxylic acid reported here is 79.1 %. It is obvious that already during the ozonolysis, which takes 90 min, the degradation of glyoxylic acid will proceed at an increasing rate. Further the prolonged action of ozone on preformed glyoxylic acid will bring about its oxidation (*vide infra*). A logical consequence was to reduce the reaction time through treating smaller amounts of maleic acid with ozone. As expected the yields of glyoxylic acid as well as of active oxygen rose until our experimental limit was reached at 99 % glyoxylic acid and 96.2 % active oxygen when the reaction time was cut down to 10 min.

A convenient method for this ozonisation could be to use a counter-current ozonisation apparatus^{9,10} where the contact time between reactants can be made very short. If the resulting solution is rapidly reduced, a high yield of glyoxylic acid may be expected.

At this point it is necessary to return to the work of Dorland and Hibbert.² As mentioned they reported a yield of 96 % glyoxylic acid. Their conditions were: 2 g of maleic acid in 35 ml 95 % formic acid was treated with ten times the theoretical amount of ozone during 5 h, *i.e.* far from an ideal procedure according to our results. We have carefully repeated Dorland and Hibbert's experiment and consistently found a yield of 42 % glyoxylic acid. Furthermore we have introduced a modification in their procedure by reducing the reaction mixture with sodium iodide and thereafter precipitating glyoxylic acid as the 2,4-dinitrophenylhydrazone. In this case 46 % of the aldehydoacid was found while 0.5 % active oxygen was present. A yield below 50 % implies that ozone during the long reaction time must have degraded glyoxylic acid. Verification of this was obtained through ozonising a solution of glyoxylic acid in concentrated formic acid. In the course of 90 min about 18 % of the material was oxidised.

Several of the ozonisation experiments on maleic acid in 98–100 % formic acid were repeated with fumaric acid. Within the limits of experimental errors (in part due to the slight solubility of fumaric acid), the results with this acid were identical with those recorded for maleic acid, quantitatively as well as qualitatively. Usually a *trans*-olefin reacts faster with ozone than the *cis*-isomer, but our investigations do not allow us to conclude that fumaric acid reacts appreciably faster than maleic acid. Some ozonisation experiments were made with maleic acid in glacial acetic acid containing 2 % perchloric acid. Neither in this case was it possible to isolate any volatile peracid. A typical ozonisation gave 84.3 % glyoxylic acid and 69.2 % active oxygen (calc. 68.6 %) of which 53.8 % was "peracid".

EXPERIMENTAL

Ozonisation technique. The ozonolyses were performed by passing an oxygen stream containing 3–4 vol. % ozone through the reaction mixture at about 3°C. The ozone output from the generator as well as unreacted ozone in the effluent gas was determined iodometrically. A gas-washing bottle with a fritted disc just above the gas inlet served as a reaction vessel. When the ozonisation was finished the electrical current was cut off and dissolved ozone removed with oxygen.

Table 4.

Strength of formic acid, %	Dissolved derivative, mg
0	60
10	68
20	78
40	101
60	118
80	138
90	150
98–100	165

Materials. The formic acid was Merck, analytical reagent. Glacial acetic acid: Riedel-de Haën, analytical reagent. Maleic and fumaric acids: British Drug Houses products, recrystallised in this laboratory.

Determination of glyoxylic acid. A 20 ml aliquot of the reaction mixture was reduced with sodium iodide and the liberated iodine removed by titration with standard thio-sulphate. The solution was then transferred quantitatively to a boiling mixture of conc. hydrochloric acid (30 ml) water (160 ml) and 2,4-dinitrophenylhydrazine (1.2 g). After 24 h the precipitate was collected, dried and weighed. The derivative had m.p. 190–192°C. (Found: C 38.0; H 2.5; N 22.2. Calc. for $C_8H_6N_4O_6$: C 37.8; H 2.4; N 22.1). It was, however, not entirely insoluble in the solution from which it was precipitated and therefore a correction had to be applied. This correction was found in the following way:

Table 5.

Concentration of formic acid, %	Glyoxylic acid, g		Total act. ox.		Peracid	
			ml 0.01 N thiosulphate per 5 ml sample			
10	0.690	0.684	11.3	12.0		
	0.696	0.677	11.8	11.9		
20	0.723	0.714	15.8	15.2		
	0.713	0.717	15.5	16.1		
40	0.806	0.810	23.5	25.5		
	0.817	0.809	23.7	24.3		
60	0.874	0.876	27.5	27.8		
	0.857	0.859	26.9	28.0		
80	0.903	0.889	35.1	34.2	23.2	23.2
	0.903	0.908	33.1	33.8	22.3	22.8
90	0.967	0.959	40.0	39.0	32.0	32.1
	0.974	0.962	39.8	39.6	32.0	32.7
98–100	1.007	1.015	50.0	51.0	48.7	49.7
	1.004	1.007	52.5	52.6	50.0	51.0

Table 6.

Maleic acid, g	Formic acid, ml	Ozonisation time, min	Glyoxylic acid, g		Total act. ox.		Peracid	
					ml 0.01 N thiosulphate per 4 ml sample			
0.500	100	45	0.608	0.603	29.7	30.5	29.4	29.2
			0.615	0.612	29.1	29.5	28.9	29.1
0.250	50	22.5	0.307	0.308	15.7	15.3	15.2	14.8
			0.307	0.308	15.5	15.6	15.3	15.3
0.125	25	11.3	0.158	0.159	8.3	8.3	8.1	8.1
			0.158	0.158	8.3	8.3	8.1	8.0

Conc. hydrochloric acid (30 ml) and water (160 ml) were heated to the boiling point; to this were added 20 ml of formic acid of the concentrations used in the ozonisations and a weighed amount of pure glyoxylic acid dinitrophenylhydrazone. The mixture was stirred vigorously, left overnight and the undissolved substance collected and weighed. A good linear relationship was obtained between the concentration of the formic acid and the amount of dissolved derivative. The results are summarised in Table 4.

Determination of active oxygen. Total active oxygen was determined by running aliquots of the reaction mixture into sodium iodide in glacial acetic acid under a carbon dioxide atmosphere. The mixture was kept in the dark for 45 min and the liberated iodine titrated with standard thiosulphate. Peracid was also determined iodometrically. The samples were run into aqueous potassium iodide to which some titanium reagent had been added in order to bind any hydrogen peroxide which might be present.¹¹ A peracid reacts rapidly and completely with aqueous iodide and can thus be distinguished from most other peroxidic compounds.

Determination of formic acid and carbon dioxide. Formic acid was determined by distilling *in vacuo* an aliquot of the reaction mixture (after ozonisation in water) and collecting the distillate in standard sodium hydroxide. Excess sodium hydroxide was backtitrated with standard hydrochloric acid. Carbon dioxide was determined by absorbing it in soda-asbestos from the gas leaving the reaction vessel. The oxygen was purged for carbon dioxide before it entered the ozone generator. Unreacted ozone was removed by passing the gas through aqueous potassium iodide, and the gas was dried by concentrated sulphuric acid and magnesium perchlorate. Towards the end of the reaction the solution of potassium iodide was acidified. The method probably gives somewhat low results.

Table 7.

Conc. of formic acid, %	Glyoxylic acid, g
10	0.648
20	0.657
40	0.678
60	0.680
80	0.700
90	0.724
98-100	0.751

Table 8.

Fumaric acid, g	Formic acid, ml	Ozonisation time, min	Glyoxylic acid, g		Total act. ox.		Peracid	
					ml 0.01 N thiosulphate per 4 ml sample			
1.00	100	90	0.951	0.963	46.0	45.6	44.0	43.7
			0.965	0.977	45.0	45.2	43.8	43.5
0.500	100	45	0.599	0.603	29.1	28.6	28.1	27.6
			0.607	0.615	28.6	27.6	27.1	27.5
0.250	50	22.5	0.306	0.311	15.1	15.3	15.0	15.1
			0.305	0.310	15.5	15.4	15.1	15.0
0.125	25	11.3	0.157	0.159	8.3	8.3	8.1	8.1
			0.158	0.159	8.4	8.4	8.2	8.1

Ozonolysis in aqueous solution. Maleic acid (1.000 g) in distilled water (100.0 ml solution) was ozonised for 55 min (2.15 g O₃/h). Carbon dioxide: a) 0.299 g; b) 0.280 g; c) 0.281 g; d) 0.286 g. Total active oxygen (ml 0.01 N thiosulphate consumed by 5.00 ml samples): a) 5.0; b) 4.8; c) 4.7; d) 4.9. Glyoxylic acid; a) 0.449 g; b) 0.438 g; c) 0.446 g; d) 0.450 g. Formic acid: a) 0.398 g; b) 0.428 g; c) 0.399 g; d) 0.399 g.

Ozonolysis in formic acid. Maleic acid (1.000 g) in the appropriate formic acid (100.0 ml solution) was ozonised for 90 min (2.15 g O₃/h). The numerical results are collected in Table 5.

Results from the series of ozonolyses with smaller amounts of maleic acid are recorded in Table 6. 98–100 % formic acid was used in all experiments.

Repetition of Dorland and Hibbert's experiment. Maleic acid (2.000 g) was dissolved in formic acid (35 ml, 95 %) and ozonised at about 0°C for 5 h with ozonated oxygen at a rate of 1.64 g O₃/h. The reaction mixture was distilled at 12 mm Hg and 20°C, and the residue was boiled with water (30 ml) for 30 min and diluted to 100 ml. Samples of this solution were precipitated with 2,4-dinitrophenylhydrazine in dilute hydrochloric acid. The solubility of the derivative in the reaction mixture was determined and corrected for. Glyoxylic acid found: a) 1.272 g, b) 1.268 g, c) 1.267 g. A modification of this procedure was introduced in the following way: After ozonisation the reaction mixture was diluted to 100 ml and 20 ml aliquots were reduced with sodium iodide. After this point the procedure was as described under the determination of glyoxylic acid. Glyoxylic acid found: a) 1.275 g, b) 1.281 g, c) 1.278 g. Total active oxygen (ml 0.01 N thiosulphate per 5 ml sample): a) 0.4 ml, b) 0.3 ml, c) 0.5 ml.

Content of glyoxylic acid after the active oxygen is consumed. 1.000 g of maleic acid was ozonised as usual, but the reaction mixture was left at room temperature until the oxygen activity had disappeared. Glyoxylic acid was then determined. Results for different concentrations of formic acids are recorded in Table 7.

Ozonolysis of fumaric acid. The reaction and the analytical determinations were performed exactly as described for maleic acid. Results are summarised in Table 8.

Ozonisation in acetic acid. Maleic acid (1.000 g) in glacial acetic acid containing 2 % perchloric acid (100 ml) was ozonised for 90 min (2.15 g O₃/h). The quantitative determinations were performed as before. A new correction factor for the solubility of glyoxylic acid 2,4-dinitrophenylhydrazone had to be worked out. The end-point in peracid titrations was not as sharp as in formic acid. Glyoxylic acid: a) 1.267 g, b) 1.269 g, c) 1.268 g, d) 1.269 g. Total active oxygen (ml 0.01 N thiosulphate per 5 ml sample): a) 60.7, b) 58.0, c) 60.5, d) 59.5. Peracid (ml 0.01 N thiosulphate per 5 ml sample): a) 45.7, b) 47.0, c) 46.2, d) 46.5.

REFERENCES

1. Harries, C. D. *Untersuchungen über das Ozon und seine Einwirkung auf organische Verbindungen*, J. Springer Verlag, Berlin 1916.
2. Dorland, R. M. and Hibbert, H. *Can. J. Res.* **18** (1940) 30.
3. Briner, E. and Franck, D. *Helv. Chim. Acta.* **21** (1938) 1297, 1312.
4. Bernatek, E. and Ledaal, T. *Tetrahedron Letters* **26** (1960) 30.
5. Bernatek, E. *Ozonolyses in the Naphthoquinone and Benzofuran Series*, Oslo University Press 1960.
6. Bernatek, E., Ledaal, T. and Solbjør, T. *To be published*.
7. Noller, C. R., Carson, J. F., Martin, H. and Hawkins, K. S. *J. Am. Chem. Soc.* **58** (1936) 24.
8. Criegee, R. and Wenner, G. *Ann.* **564** (1949) 9.
9. Pummerer, R. and Richtzenhain, H. *Ann.* **529** (1937) 50.
10. Bernatek, E. and Valen, K. *Acta Chem. Scand.* **14** (1960) 224.
11. Ledaal, T. and Bernatek, E. *Anal. Chim. Acta* **28** (1963) 322.

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