ACTA CHEMICA SCANDINAVICA 16 (1962) 2421–2428

Ozonolysis of Phenols

III. 1- and 2-Naphthol

ERLING BERNATEK and CARLY FRENGEN

Universitetets Kjemiske Institutt, Blindern-Oslo, Norway

1- and 2-naphthol have been ozonised in ethyl acetate at 3–4°. The ozonolysis fragments, carbon dioxide, formic, oxalic, *o*-carboxylcinnamic, *o*-formylcinnamic, phthalic, and phthalaldehydic acids as well as phthalaldehyde have been determined quantitatively. Combinations of common ozonolysis reactions types are proposed to explain qualitative and quantitatives results.

In our previous papers [1,2] in this series we have discussed the fate of some simple phenols when exposed to the action of ozone. It was found that the degradation products for the greater part consisted of rather small molecules such as carbon monoxide and dioxide, formic and oxalic acids, and some glyoxal. In the case of the dihydric phenols, catechol, resorcinol and quinol, there was a certain amount of products which remained unidentified, mainly because of their labile and untractable character. By introducing a relatively inert aromatic nucleus, as in 1- and 2-naphthol, it was hoped to obtain degradation products, which more easily could be isolated and identified. As will be seen from the present paper these expectations have been fulfilled and, especially in the case of 2-naphthol, the distribution of the carbon from the starting material can be accounted for in detail.

Dissolved in ethyl acetate both phenols absorbed ozone readily. The two first moles were consumed quantitatively, but after that point ozone escaped in increasing amounts. The total ozone consumption would probably have been large, leading to the complete destruction of the compounds under investigation. The experiments recorded here, however, are only concerned with the reactions which take place when one or two moles of ozone are applied.

After the ozonisation the solutions contained active oxygen and for both phenols in amounts corresponding roughly to half the absorbed ozone. The nature of the peroxidic compounds has not been investigated closely, but the existence of an ozonide cannot be excluded since hydrogen peroxide was formed by hydrolysis. On the other hand, the active product is remarkably stable only losing a few per cent of the activity in twenty-four hours. During this time traces of carbon monoxide were evolved. Small amounts of carbon dioxide were formed during the ozonisation.

Table 1. Reaction products from ozonolysis of 1- and 2-naphthol with 2 moles of ozone.

Reaction product	1-Naphthol moles/mole	1-Naphthol % recovered C	2-Naphthol moles/mole	2-Naphthol % recovered C
CO_2 (ozonolysis)	0.09	2.6	0.09	10.8
CO_2 (hydrolysis)	0.17		0.99	
Formic acid	1.80	17.8	0.92	9.2
Oxalic acid	—	—	0.04	0.9
o-Carboxylcinnamic acid	—	—	0.23	22.6
o-Formylcinnamic acid	—	—	0.15	15.2
Phthalaldehydic acid	(0.40)	(32)	—	—
Phthalic acid	0.59	46.6	0.15	11.9
Phthalaldehyde	—	—	0.34	27.1

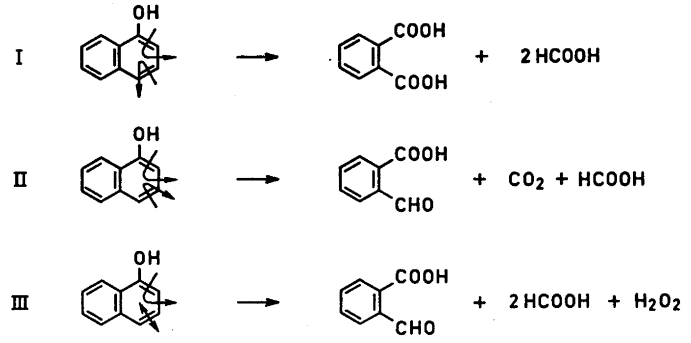
The ozonisation mixture was treated with water at room temperature until the active oxygen had disappeared from the ethyl acetate layer. The aqueous layer gave initially a yellow coloration with titanium reagent, indicative of hydrogen peroxide. Further amounts of carbon dioxide were evolved during hydrolysis. From the aqueous layers were isolated formic and oxalic acids, while the ethyl acetate layer afforded *o*-carboxylcinnamic, *o*-formylcinnamic, phthalaldehydic and phthalic acids beside phthalaldehyde. The results from the quantitative determinations of these compounds are summarised in Table 1.

The values for phthalaldehydic acid are only tentative as this compound could not be determined directly. The mixture of non-volatile ozonolysis products from 1-naphthol were analysed for carbon and 78.9 % of the original carbon were found here. Together with the carbon recovered in the volatile compounds carbon dioxide and formic acid, this adds up to a carbon balance of 99.3 %. Phthalaldehydic acid is thus regarded as the difference between the total nonvolatile matter and phthalic acid. Probably this difference also encompasses minor amounts of unidentified products. Summation of the recovered carbon from 2-naphthol gives a carbon balance of 97.7 %. A determination of carbon content in the dry matter from this phenol amounts to 78.3 %, which together with the carbon from volatile products gives a carbon balance of 98.3 %.

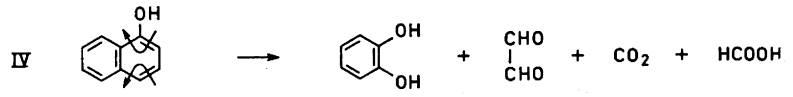
From Table 1 it will be seen that the aromatic ozonolysis products from 1-naphthol evidently are the result of a reaction with two molecules of ozone since only two carbon atoms are left of the phenolic ring. Further the "aromatic balance" (*i.e.* the percentage of recovered aromatic ring per mole of naphthol) is excellent: 99 %. This is indicative of an exclusive attack on the hydroxylated ring leaving the unsubstituted ring intact. 1-Naphthol can of course be split up by ozone in a number of ways. If we take into account the three usual modes of ozonolysis, anomalous ozonolysis, acid-rearrangement and hydrolysis of an ozonide, at least 19 reaction combinations are theoretically possible. Only three of these are necessary, however, to explain our qualitative and quantitative results in a satisfactory way. If we use our customary shorthand for the reaction types:

anomalous ozonolysis acid-rearrangement hydrolysis of ozonide

we can represent the pertinent reaction combinations in the following way:



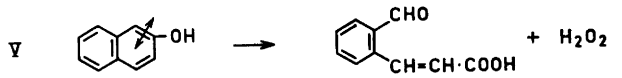
The bond adjacent to the hydroxyl group is probably attacked first and we have here in all three reaction schemes the same type of anomalous ozonolysis. This is to be expected in a bond of this type. At the other bond in question the attack evidently takes another course: acid-rearrangement which can take either course as in I and II or the formation of an ozonide with subsequent hydrolysis. Assuming that 59 % of the 1-naphthol follows scheme I, 26 % follows II and 15 % III, one gets the following quantitative distribution of reaction products in moles per mole of naphthol: Phthalic acid 0.59, phthalaldehydic acid 0.41, carbon dioxide 0.26, formic acid 1.74, hydrogen peroxide 0.15, in good agreement with the results in Table 1. It is noteworthy that no phenolic compound can have been formed in any appreciable amount as would have been the case if anomalous ozonolysis had taken either or both courses in scheme IV.



Finally we shall briefly discuss the oxygen balance. The number of oxygen atoms in the reaction products per mole of starting material is 7.98 (if we take into account the assumed 0.15 moles of hydrogen peroxide). On the side of reactants we have one atom of oxygen in the naphthol, six in the applied ozone and 1.15 in the water necessary for hydrolysis of the primary ozonisation products, which is 8.15 atoms in all and in fair agreement with the experimental results.

2-Naphthol gives relatively large amounts of the mono-ozonolysis products *o*-formylcinnamic acid *o*-carboxylcinnamic acids, which can be caused by a more tardy reaction of these compounds with ozone or by the consumption of ozone in side-reactions not leaving enough for complete cleavage of the phenolic ring. The aromatic balance points in this latter direction as it amounts only to 87 % indicative of a certain degradation of the entire naphthalene

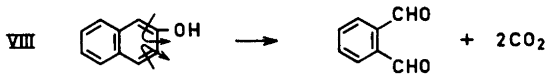
ring system. Theoretically 2-naphthol can be split up by one molecule of ozone in nine different ways and by two molecules in nineteen ways (attack on the phenolic ring only), but only a limited number are necessary to explain the experimental results. Mono-ozonolysis seems exclusively to have taken place at the bond adjacent to the hydroxyl group, which is to be expected since this bond as in the case of 1-naphthol probably is attacked first. The only likely formation of the cinnamic acid derivatives is through a hydrolysis of ozonide and acid-rearrangement as in V and VI, respectively.



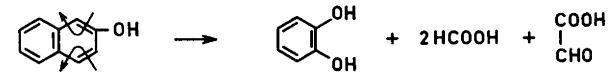
Phthalic acid can simply be formed through a double acid-rearrangement:

This leaves us with one molecule of glyoxylic acid, a substance which has not been detected among the reaction products. Glyoxylic acid, however, would react readily with hydrogen peroxide present in the hydrolysis mixture and become oxidised to carbon dioxide and formic acid.

Phthalaldehyde can theoretically be formed in five different ways two of which give identical products. As the main reaction we regard the following cleavage:



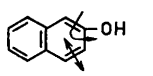
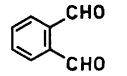
Through the mentioned four reaction schemes the experimental results can be explained qualitatively but still not quantitatively. The low value for the aromatic balance implies a reaction of the following type:



Catechol is readily attacked by ozone, the ozonolysis having been investigated by one of the present authors [2]. It was found that the dihydric phenol mainly was split up into formic acid and carbon dioxide while oxalic acid and glyoxal occurred in lesser amounts.

Assuming that 15 % of 2-naphthol is ozonolysed according to V, 23 % according to VI, 15 % according to VII, 34 % according to VIII and 13 % according to IX (with subsequent cleavage of catechol as previously described [2]), we arrive at the following distribution of reaction products in moles per mole of naphthol: Carbon dioxide 1.15, formic acid 0.79, *o*-formylcinnamic

acid 0.15, *o*-carboxylcinnamic acid 0.23, phthalic acid 0.15 and phthalaldehyde 0.34. Due to the chosen percentages of the different reactions the amounts of aromatics of course fit the experimental data exactly. On the other hand the value for carbon dioxide is too high and that for formic acid too low. Participation to a small extent of reaction X where less carbon dioxide is produced than in VIII and in addition one molecule of formic acid is formed, could give a very close agreement with the experiments.

X   + CO_2 + HCOOH + H_2O_2

Oxalic acid is assumed to result from the degradation of catechol only, which gives an amount of about 0.025 moles as compared with the value in Table 1 of 0.04 moles.

Ozone consumption also need some comment since appreciable amounts mono-ozonolysis products are found. These products correspond to 38 % of the starting material, which could mean that 0.38 moles of the applied ozone have not reacted. If catechol is formed in an amount of 0.13 moles this will consume three molecules of ozone per molecule, *i.e.* in all 0.39 moles, which fits in nicely with the above mentioned value.

In checking the oxygen balance we find that ozonolysis products contain 6.8 atoms of oxygen per mole of starting material. The phenol contains one oxygen atom and the applied ozone six, in all seven atoms. Our chosen reaction paths require that some water enter into this balance. VIII will lead to the formation of one molecule of water, *i.e.* totally 0.34 moles. IX would need two moles of water for hydrolysis of primary products, in our case 0.26 moles. The further degradation of catechol requires one molecule, *i.e.* 0.13 moles. This is a negative balance of 0.05 moles, which does not materially affect our previous value. The water needed for formation of hydrogen peroxide in V and X do not enter the account as the peroxide is consumed in the oxidation of glyoxylic acid.

Ozonolysis with one mole of ozone led to the identification of no new compounds, but the relative amounts of the products were quite different

Table 2. Reaction products from ozonolysis of 1- and 2-naphthol with 1 mole of ozone.

Reaction product	1-Naphthol moles/mole	1-Naphthol % recovered C	2-Naphthol moles/mole	2-Naphthol % recovered C
CO_2 (ozonolysis)	—	—	—	—
CO_2 (hydrolysis)	0.05	0.5	0.16	1.5
Formic acid	0.85	8.5	0.53	5.2
Oxalic acid	—	—	—	—
o-Carboxylcinnamic acid	0.14	11.5	0.27	27.0
o-Formylcinnamic acid	—	—	0.52	51.8
Phthalaldehydic acid	+	+	—	—
Phthalic acid	—	—	—	—
Phthalaldehyde	—	—	0.03	2.4
Naphthol	+	+		17.5

from the previous results. Only for 2-naphthol a quantitative analysis has been carried out and even here the carbon balance is only 90 % due to the occurrence of some tarry matter. The analysis for carbon in the total non-volatile matter indicates that the percentage of recovered carbon actually is about 97. The same procedure gave for 1-naphthol a carbon balance of about 93 %. As expected certain amounts of unreacted naphthols also were found.

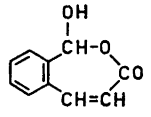
The values for 2-naphthol are calculated in relation to the amount of reacted material (82.5 %). This is not possible in the case of 1-naphthol since unreacted material has not been determined; the values refer to the initial amount of naphthol and are consequently too low.

A conspicuous feature in the mono-ozonolysis of 2-naphthol is the formation of rather large amounts of *o*-formylcinnamic acid and small amounts of phthalaldehyde as compared with the results in Table 1. It seems that *o*-formylcinnamic acid is a precursor for phthalaldehyde, which is compatible with the reaction schemes already proposed. If, as in V, an ozonide is formed at the 1,2-bond this can rearrange in the direction of the 2,3-bond and the reaction thus becomes indistinquishable from the anomalous ozonolysis indicated in VIII or X. The 3,4-bond can then be attacked with subsequent acid-rearrangement or formation of ozonide. A certain amount of rearrangement of ozonide is indeed to be reckoned with as the content of active oxygen after the ozonolysis is much greater than is inherent in the different reaction schemes presented in this paper. The absence of phthalic acid is countered by the increased amount of *o*-carboxylcinnamic acid even if the increase is not so great as could be expected. Reaction scheme VI explains this as it in the initial stage is a precursor for reaction VII.

The carbon balance for mono-ozonolysis of 2-naphthol is not too good, only about 88 %, while elemental analysis for carbon in the sum of non-volatile products leads to a total carbon balance of 97 %.

A new feature in Table 2 is the formation of *o*-carboxylcinnamic acid from 1-naphthol in quite considerable amounts. It can be a precursor for phthalic as well as phthalaldehydic acid.

Wiley and Hobson [3] prepared in 1949 *o*-formylcinnamic acid by a Perkin condensation of phthalaldehyde and malonic acid in the presence of pyridine. Their product had m.p. 163—164°C, while the substance we have designated *o*-formylcinnamic acid has m.p. 124—125°C. The formation of the latter compound from a cyclic compound with a mild reagent like ozone followed by a cautious working-up procedure strongly suggest that it is the *cis*-compound, *o*-formyl-*allo*-cinnamic acid. On the other hand the acid from the Perkin reaction must be the *trans*-compound. The difference in melting points can well be explained by this assumption. As mentioned in the experimental part, the infra-red spectrum shows a carbonyl absorption at 1700 cm^{-1}. This is indicative of a lactol carbonyl in a strain-free ring. A lactol form of the acid as XI is therefore very probable and confirmed by the hydroxyl absorption at 3200 cm^{-1}. Only the *cis*-form can possibly form such a lactol.

XI 

EXPERIMENTAL

Ozonolysis. The ozonisation technique and the decomposition with water are described in a preceding communication [1].

Ozone absorption was measured by leading the effluent gases into aqueous potassium iodide, which was changed every third minute and the liberated iodine titrated. Until about 1.8 moles of ozone per mole of naphthol had been applied, virtually no ozone escaped and when 2.17 moles had been applied 2.12 moles had been absorbed in the case of both naphthols. Of 2.79 moles 2.58 moles were absorbed by 1-naphthol and 2.63 moles by 2-naphthol.

Active oxygen was determined by pipetting aliquots of the ozonised solution into sodium iodide in glacial acetic acid and titrating liberated iodine. 1-Naphthol gave 0.63 and 2-naphthol 0.52 g atoms active oxygen per mole of starting material. After standing for 24 h both solutions contained 0.48 g atoms of active oxygen.

Determination of products. The determinations of carbon dioxide during ozonisation and decomposition, formic and oxalic acids were performed as before [1]. Volatile products were determined from ozonolysis of 1 g of naphthol and non-volatile products from 10 g.

A. 1-Naphthol

(*a*) With 1 O_3: Carbon dioxide during ozonisation nil, during hydrolysis 14, 15, 17, and 12 mg. Formic acid 259, 291, 276, and 257 mg. Oxalic acid nil.

(*b*) With 2 O_3: Carbon dioxide during ozonisation 29, 30, 28, and 29, during hydrolysis 54, 55, 46, and 48 mg. Formic acid 706, 553, 552, and 467 mg. Oxalic acid nil.

B. 2-Naphthol

(*a*) With 1 O_3: Carbon dioxide during ozonisation nil, during hydrolysis 42 41, 40, and 41 mg. Formic acid 106, 157, 157, and 135 mg. Oxalic acid nil.

(*b*) With 2 O_3: Carbon dioxide during ozonisation 40, 21, 24, 33, 28, and 33 mg, during hydrolysis 275, 328, 279, 314, 299, 311, and 277 mg. Formic acid 329, 230, 302, and 319 mg. Oxalic acid 266, 288, and 286 mg.

o-*Carboxylcinnamic acid.* This acid was found in the ethyl acetate layer after hydrolysis of the ozonisation mixture. The ester phase was extracted with aqueous sodium bicarbonate and the extract acidified with concentrated hydrochloric acid to pH *ca.* 1. In some cases a small precipitate was formed at this point. The acidified solution was extracted with ethyl acetate and the extract dried and evaporated. The residue was extracted with boiling water and the undissolved part was combined with the material immediately separating from the aqueous extract. Recrystallisation first from acetone-carbon tetrachloride and thereafter from large amounts of water (charcoal) gave a white, crystalline substance with m.p. 192°C. (Found: C 62.4; H 4.1; *E* 96. Calc. for $C_{10}H_8O_4$: C 62.5; H 4.2; E_{dibasic} 96.) The precipitates from the acidified bicarbonate extracts contained mainly this substance. $C_{10}H_8O_4$ decolorised permanganate instantaneously. The infra-red spectrum (Nujol) showed the following absorption bands: Carboxyl group 3300—2200, 1690, 1280, and 920 cm^{-1}. C—C double bond in conjugation with the aromatic nucleus 1631 cm^{-1}. Aromatic absorption 1601, 1576, and 1487 cm^{-1}. *Ortho*-disubstitution 758 cm^{-1}.

Yields: 1-Naphthol (1 O_3) gave 1.84 g. 2-Naphthol (1 O_3) gave 2.96 g, (2 O_3) 3.07 and 3.01 g.

o-*Formylcinnamic acid.* The aqueous extract from the above experiment was, after separation of *o*-carboxylcinnamic acid, extracted with ethyl acetate. This extract was in turn extracted with a small amount of concentrated aqueous sodium bicarbonate, which upon acidifying with 6 N hydrochloric acid to pH ca. 4 gave a white precipitate. Recrystallised from water (charcoal), m.p. 124—125°C. Long white needles. (Found: C 67.9; H 4.7; *E* 177. Calc. for $C_{10}H_8O_3$: C 68.2; H 4.5; *E* 176). The substance gave a 2.4-dinitrophenylhydrazone, which recrystallised from alcohol had m.p. 214°C (decomp.) (Found: C 54.2; H 3.4; N 15.7. Calc. for $C_{16}H_{12}N_4O_6$: C 53.9; H 3.4; N 15.7). Some $C_{10}H_8O_3$ was

contained in the precipitates from the acidified bicarbonate solution mentioned in the foregoing experiments. The infra-red spectrum (KBr-pellet) showed the following absorption bands: Hydroxyl 3200 cm^{-1}. Conjugated lactone (lactol) carbonyl in strain-free ring 1700 cm^{-1}. Conjugated double bond and α,β-unsaturated ester 1642 and 821 cm^{-1}, respectively. Aromatic absorption 1600 and 1570 cm^{-1}. *Ortho*-disubstitution 745 cm^{-1}. Yields: 2-Naphthol (1 O_3) gave 5.22 g, (2 O_3) 1.86 g.

Phthalaldehyde. The ethyl acetate layer, which after the hydrolysis had been exhaustively extracted with saturated aqueous sodium bicarbonate, was dried and evaporated. Light yellow oil, which for the greater part crystallised and consisted of fairly pure phthalaldehyde. A sample was sublimated at 50 – 60°C and 10 mm Hg. Light yellow needles, m.p. 54 – 56°C, which gave a precipitate with 2,4-dinitrophenylhydrazine, reduced Tollens' and Schiff's reagents and gave a characteristic green coloration of the skin. (Found: C 71.6; H 4.6. Calc. for $C_8H_6O_2$: C 71.6; H 4.5). The substance was readily oxidised to phthalic acid by Beckmann's reagent. Further amounts of phthalaldehyde were found in the aqueous decomposition solution and isolated by extraction with ether. This fraction contained traces of *o*-carboxylcinnamic and oxalic acids. Yields: 2-Naphthol (1 O_3) gave 0.23 g, (2 O_3) from ethyl acetate 1.77, 1.57, 1.86, and 1.83 g, from water 1.42 and 1.36 g.

Phthalaldehydic acid. After the hydrolysis the ethyl acetate layer was evaporated to dryness and the residue extracted with chloroform. The extract left upon evaporation a crystalline substance which was sublimated *in vacuo*. Small white crystals, m.p. 88°C. (Found: C 63.4; H 4.1. Calc. for $C_8H_6O_3$: C 64.0; H 4.0). The sublimate evidently consisted of somewhat impure phthalaldehydic acid. It easily formed an oxime with m.p. 120°C, undepressed on admixture with an authentic sample. 2,4-Dinitrophenylhydrazone, m.p. 255°C. (Found: C 50.8; H 3.3; N 16.2. Calc. for $C_{14}H_{10}N_4O_6$: C 50.9; H 3.3; N 17.0). The sample with m.p. 88°C was subjected to repeated sublimations *in vacuo* and thereafter identified as phthalaldehydic acid by its infra-red spectrum. In substance phthalaldehydic acid was isolated only from the ethyl acetate after ozonolysis of 1-naphthol with two moles of ozone while it was identified through its oxime in the aqueous layer. Likewise after ozonolysis of 1-naphthol with one mole of ozone, the acid was identified through the oxime.

Phthalic acid. The acid filtrate from the isolation of *o*-formylcinnamic acid was exhaustively extracted with ether and the collected extracts dried and evaporated. A crystalline mass resulted, which was triturated with chloroform leaving a greyish crystalline substance. Recrystallised from acetone-carbon tetrachloride and water. White crystals. M.p. 192°C alone and in admixture with an authentic sample of phthalic acid. The identity of the substance was confirmed by its infra-red spectrum. (Found: *E* 84. Calc. for $C_8H_6O_4$: 83). Yields: 1-Naphthol (2 O_3) gave 6.71 g and 2-naphthol (2 O_3) 1.83, 1.60 g.

Unreacted naphthols. (*a*) 1-Naphthol. The ethyl acetate after treatment with water and extraction with aqueous sodium bicarbonate was evaporated. The resulting syrupy mass was dissolved in sodium hydroxide (2 N), diluted with water and acidified with hydrochloric acid. The violet precipitate was recrystallised from dilute alcohol and sublimated *in vacuo*. Long colourless crystals. M.p. 88 – 90°C alone and mixed with an authentic specimen of 1-naphthol.

(*b*) 2-Naphthol. After evaporation of the ethyl acetate as in the above experiment the resulting mass was sublimated *in vacuo* (1 mm Hg) at 100 – 110°C and afforded a white crystalline substance. Recrystallised from water. M.p. 121°C alone and in mixture with an authentic specimen of 2-naphthol. The picrate had m.p. 155°C, undepressed in mixture with 2-naphthol picrate. Yields: 1.76, 1.72, and 1.75 g.

The authors' thanks are due to Mag. sc. Else Augdahl for the determination of infra-red spectra.

REFERENCES

1. Bernatek, E. and Frengen, C. *Acta Chem. Scand.* **15** (1961) 471.
2. Bernatek, E., Møskeland, J. and Valen, K. *Acta Chem. Scand.* **15** (1961) 1454.
3. Wiley, R. H. and Hobson, P. H. *J. Am. Chem. Soc.* **71** (1949) 2429.

Received June 6, 1962.