

CHEMISTRY

ON THE OZONIZATION OF NAPHTHALENE AND 2,3-DIMETHYL-NAPHTHALENES IN CONNECTION WITH THE STRUCTURE OF THE RING SYSTEM

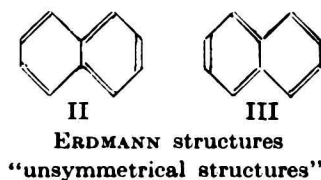
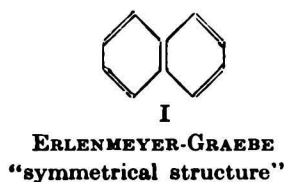
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(communicated at the meeting of Sept. 30, 1950)

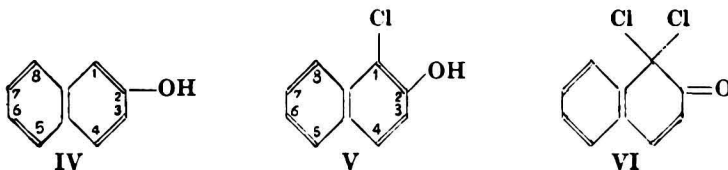
§ 1. Introduction

The classical structural theory of the organic chemistry mainly discusses the following valency structures for naphthalene:



On the strength of the chemical behaviour of naphthalene derivatives MARCKWALD [1] assumed that the naphthalene ring reacts exclusively according to structure I. This view was supported by later investigations of FRIES [2] and of FIESER [3] and their collaborators.

The argumentation is based among other things on the behaviour of β -naphthol (IV) in substitution reactions. Introduction of the chlorine atom into β -naphthol leads to the formation of: 1-chloro-2-hydroxy-naphthalene (V). Introduction of another chlorine atom causes the formation of dichloroketone (VI) and not of 1,3-dichloro-2-hydroxynaphthalene [4].



When β -naphthol is coupled with a diazotized amine $[\text{Ar}-\text{N} \equiv \text{N}]\text{Cl}$, the $\text{Ar}-\text{N} \equiv \text{N}$ -group is linked to carbon atom 1; if position 1 is occupied by a methyl group, no coupling takes place. The hydrogen atom in position 3 is not substituted. To account for these and a number of similar phenomena FIESER assumes that the substitution is preceded by addition to the double bond of the enolic group: $-\text{C} = \text{C}-\text{OH}$.



As the ERLÉNMEYER formula contains a double bond between carbon atoms 1 and 2, but not between 2 and 3, FIESER concludes that the naphthalene ring in β -naphthol occurs in structure IV only. Certain regularities in the substitution in β -naphthol and related compounds, which are caused by differences in reaction velocity with respect to the 1 and 3 positions, lead to a conclusion about the stationary state of the molecule. Assuming that the structure valid for the ring system of naphthalene is the same as that for β -naphthol, FIESER [5] concludes that naphthalene has the symmetrical structure suggested by ERLÉNMEYER and that the double and single bonds are fixed in the 1,2 and 2,3-positions respectively.

On the strength of extensive investigations on tricyclic compounds, which are related to naphthalene, FRIES arrives at the same conclusion, i.e. that naphthalene has little tendency to exist in the unsymmetrical form (II or III), because one of the ring systems would then have to depart from the aromatic condition and acquire the bond structure of the highly reactive o-benzoquinone.

Accurate X-ray studies by ROBERTSON have shown, however, that the distances between two adjacent carbon atoms in the six-membered rings of the naphthalene molecule are nearly all the same and equal to 1.40 Å. A rigid ERLÉNMEYER-GRAEBE structure would require a difference of about 0.20 Å between the distance of carbon atoms 1—2 and the distance of carbon atoms 2—3.

FIESER's conclusion that naphthalene has a fixed ERLÉNMEYER-GRAEBE structure is therefore unacceptable. According to the theory of resonance naphthalene is a resonance hybrid like benzene; in its ground state the molecule does not contain single or double carbon bonds; two adjacent C atoms are linked by an "aromatic carbon bond".

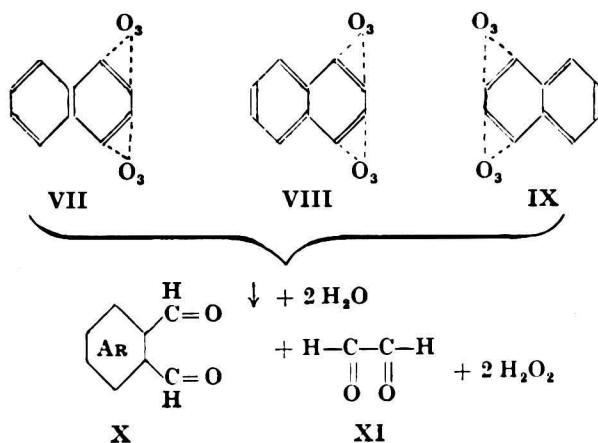
In the present paper we describe the behaviour of naphthalene and 2,3-dimethylnaphthalene towards ozone, the most characteristic reagent to the double carbon bond.

In aliphatic compounds, which contain a double carbon bond, an ozone molecule reacts with the atomic group $> C = C <$ to form an ozonide, whose structure was in one case determined by RIECHE. The way in which the oxygen atoms are bound to form ozonides, derived from aromatic hydrocarbons, is not yet known with certainty. We know that these ozonides are decomposed by water, as a result of which hydrogen peroxide is formed and the six-membered ring is broken; two adjoining carbon atoms each take up one O atom, so that the group $O = C - C = O$ is formed. During this reaction the ring structures which in the classical structural theory are designated as double bonds, are broken.

A study of the ozonolysis of naphthalene and its homologues may therefore show whether these compounds are capable of reacting according to different valency structures (I, II, III).

§ 2. Ozonolysis of naphthalene

The action of ozone on naphthalene was first investigated by HARRIES and WEISS [6], who found that an explosive diozonide $C_{10}H_8O_6$ is formed. By decomposing this diozonide with water these investigators obtained phthalaldialdehyde (X) and phthalic acid; glyoxal (XI), which might have been expected, was not found. This scission product has been identified by us. The following formulae give a schematic representation of the naphthalene diozonide; obviously, the above scission products can be formed both from the diozonide of an ERLÉNMEYER–GRAEBE structure (VII) and from a diozonide of an ERDMANN structure (VIII or IX):



SEEKLES [7], in again investigating the action of ozone on naphthalene, aimed at finding a method to prepare *o*-phthalaldehyde; he obtained it in a yield of 10 % of the theoretical value and in addition *o*-phthalaldehydic acid in a yield of 70 %, i.e. 80 % of the quantity of aromatic decomposition products to be expected.

This shows that the action of ozone on naphthalene *chiefly* results in the formation of a diozonide. This is in agreement with measurements on the rate of reaction, which we carried out in collaboration with H. BOER.

The curve in figure 1 represents the consumption of moles of ozone per mole of naphthalene as a function of the time (solvent chloroform, temperature -40°C).

The rate of reaction drops appreciably after 2.02 moles of ozone have been taken up per mole of naphthalene. The diozonide formed continues to react very slowly with ozone, the second six-membered ring being attacked with formation of a pentozonide. The fact that the bend in the curve occurs at 2.02 moles and not at 2 moles of ozone implies that already during the first stage of the reaction some pentozonide is formed; a rough calculation shows that this quantity is about 0.01 mole.

The question arises whether a triozonide may be formed as an isolable product. This is improbable, however, because a triozonide molecule con-

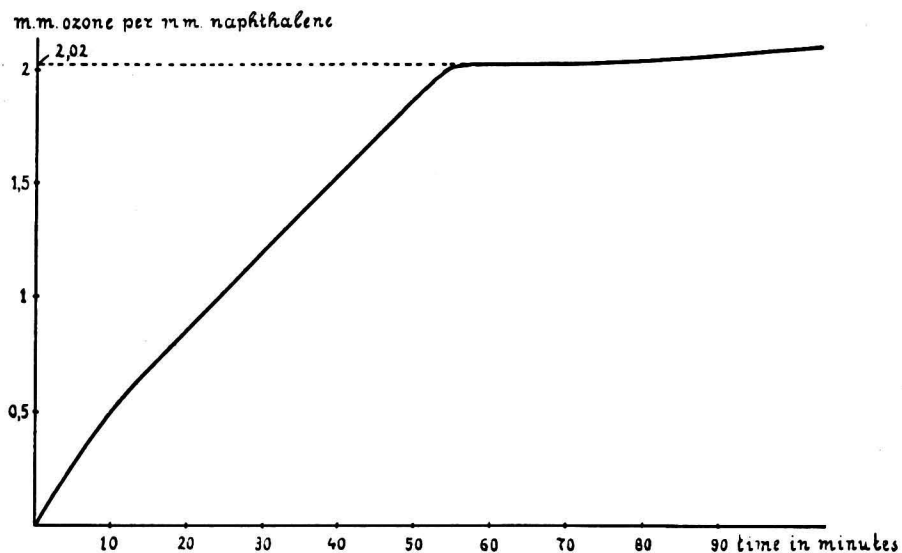
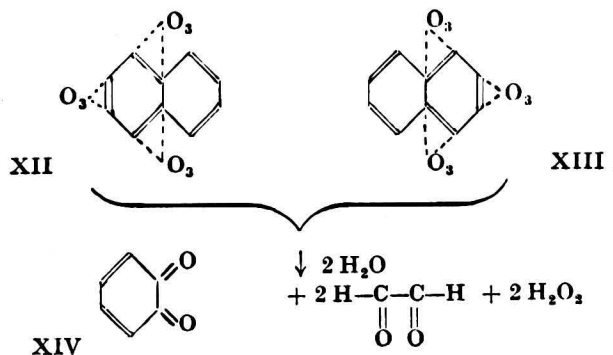


Fig. 1

tains two double carbon bonds, which will rapidly continue their reaction with ozone. Hydrolysis of a triozonide from an ERDMANN structure (XII or XIII) would yield o-quinone (XIV):



However, we found no indication of the formation of o-quinone in the ozonolysis of naphthalene.

Below follows a brief description of the experiments¹⁾ which were partly carried out in collaboration with H. BOER. For 2–4 hours ozone-containing oxygen is passed at -25°C through a solution of 13–30 millimoles of naphthalene in 30–40 ml of chloroform. The rate of flow of the gas mixture is 3.8 litres ($+20^\circ \text{C}$, 760 mm) per hour, the ozone content being 12–15 % by wt, so that each hour 13–17 millimoles of ozone is passed through.

¹⁾ Thesis of L. W. F. KAMPSCHMIDT; (Amsterdam 1950). The complete experimental data will be published in the *Recueil des Travaux Chimiques*.

After the ozonization the bulk of the chloroform is distilled off in vacuo at room temperature, the remaining solution (5 ml) being poured into pure ethyl ether cooled to -20°C . The diozonide of naphthalene precipitates and is filtered off at -20°C (glass filter) and washed with cold ether. The ethereal filtrate contains non-converted naphthalene, the quantity of which can be determined.

The ozonide, which is very explosive, is worked up in various ways. Decomposition with water yields a solution whose phthalaldehyde content is betrayed first by a deep blue colour and then by a black precipitate after addition of ammonia and acidification with acetic acid. If the ozonide is treated with a solution of hydroxylamine hydrochloride and soda, it is decomposed, the dialdehydes formed reacting with hydroxylamine. From the reaction mixture we isolated the *dioxime of glyoxal* (identified by melting point and mixed melting point) and the *mono-oxime of phthalimide* (melting point 254°C ; mixed melting point with an authentic sample showed no depression). The latter compound is formed, as has been known for a long time already, by the action of hydroxylamine on phthalaldehyde¹⁾. The question whether in the ozonolysis of naphthalene a small quantity of o-quinone is formed cannot be easily solved by experiments, because o-quinone is an unstable compound, which is decomposed by water. WILLSTÄTTER indicates that o-quinone is readily reduced to o-dihydroxybenzene by sulphurous acid. Therefore we treated the chloroform solution, as obtained after the ozonization of naphthalene, with an aqueous solution of sulphurous acid. However, we did not succeed in identifying o-dihydroxybenzene.

§ 3. *The ozonolysis of 2,3-dimethylnaphthalene*

This reaction was investigated by one of us (W.) in 1941 and 1942 in collaboration with J. VAN DIJK [8]. In this investigation, which could not be completed owing to the war conditions, only the aliphatic scission products of the ozonide were identified, i.e. dimethylglyoxal and small quantities of methylglyoxal and glyoxal.

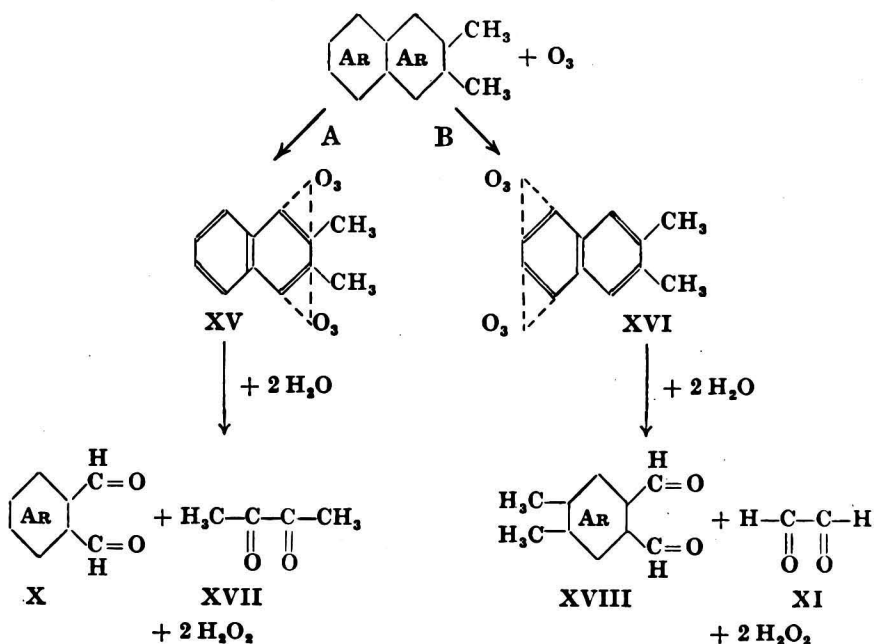
In the first place we determined the consumption of ozone per mole of dimethylnaphthalene as a function of the time. The curve obtained has the same shape as that of naphthalene (cf. fig. 1). The reaction of ozone (formation of diozonides) at -40°C proceeds rapidly until 2.04 millimoles per millimole of dimethylnaphthalene have been taken up; at this point the curve shows a sharp bend and the reaction continues to proceed very slowly (formation of pentozonide).

The investigation of the aromatic scission products shows that two isomeric diozonides (XV and XVI) are formed. In the main reaction (A) the methylated six-membered ring is attacked by ozone, as had already become probable by the investigation of WIBAUT and VAN DIJK; in

¹⁾ The chemism of this reaction will be described in a future paper.

addition, a side reaction (B) develops, in which the non-methylated six-membered ring reacts with ozone. The formation of the diozonide XXI was already assumed by KOOYMAN [9], who pointed out that this diozonide may react to form a pentozonide which, on being decomposed, yields methylglyoxal.

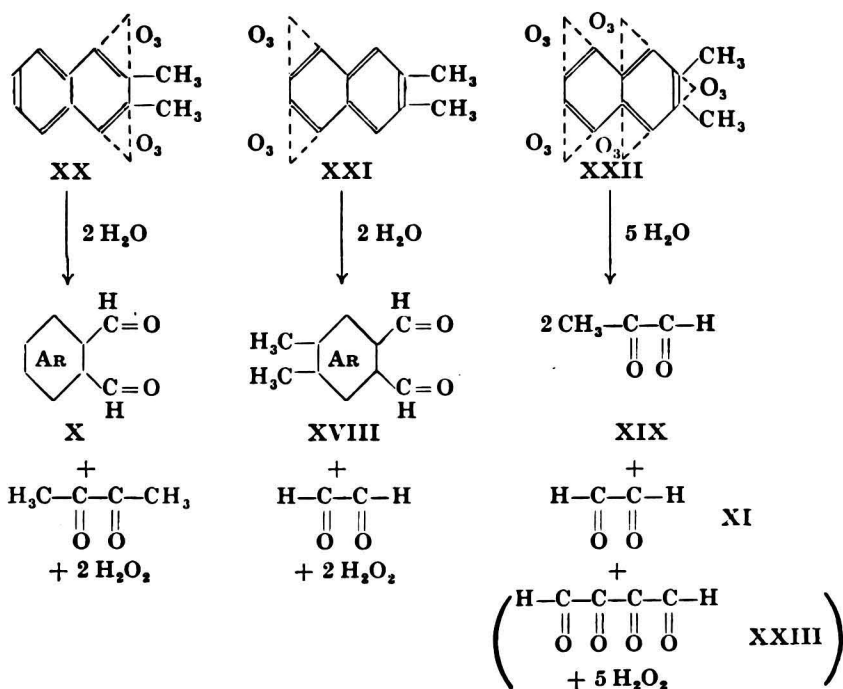
After the hydrolytic splitting of the mixture of isomeric diozonides we found as aromatic decomposition products mainly derivatives of phthalaldehyde (X) and a smaller quantity of derivatives of 4,5-dimethylphthalaldehyde (XVIII). As aliphatic scission products we found — in agreement with the observations of WIBAUT and VAN DIJK — dimethylglyoxal (XVII), glyoxal (XI) and methylglyoxal (XIX).



Phthaldialdehyde and dimethylglyoxal may be formed from the diozonide (XV), derived from the ERLLENMEYER-GRAEBE structure, but also from the diozonide (XX), derived from an ERDMANN structure. Dimethylphthalaldehyde and glyoxal may be formed from the diozonide (XVI), derived from the ERLLENMEYER-GRAEBE structure, as well as from the diozonide (XXI), derived from one of the two ERDMANN structures. Hydrolysis of the pentozonide (XXII), which may be formed from this ERDMANN structure, yields methylglyoxal (XIX), glyoxal and the hypothetical tetra-oxobutane (XXIII), which is further decomposed:

(See form. following page).

It is therefore to be expected that, as the action of ozone on dimethylnaphthalene is continued, the quantity of methylglyoxal will increase with respect to dimethylglyoxal, for in the first stage of the ozonization



almost exclusively diozonides are formed. The following experimental data are in agreement with this assumption:

TABLE I
Ozonization of 2,3 dimethylnaphthalene in chloroform at -25°C .

No.	dimethyl-naphthalene in millimoles	ozone passed through in millimoles	dimethyl-glyoxime in millimoles	methyl-glyoxime in millimoles	glyoxime in millimoles
1	50	100	4.55	0.21	0.7
2	20	300	1.9	0.19	0.66

In experiment 1, where two moles of ozone were passed through per mole of dimethylnaphthalene, the molecular ratio dimethylglyoxime: methylglyoxime = 22; in experiment 2, where 15 moles of ozone per mole of hydrocarbon were passed through, this ratio is 10. It should be observed that the quantity of dimethylglyoxime found in these experiments is only 9 % of what might have been expected according to the reaction scheme. This is caused by the fact that the dimethylglyoxal formed in the hydrolytic splitting of the ozonides is oxidized by the hydrogen peroxide, which is also formed, thus causing the formation of acetic acid. We actually found in experiments 1 and 2 acetic acid in yields of 70 and 75 % respectively of the quantities calculated on dimethylnaphthalene. Oxidation of methylglyoxal may yield acetic acid in addition to formic acid. However, only traces of formic acid were found; this acid was possibly further

decomposed in the oxidizing medium. The values found for the ratio dimethylglyoxime : methylglyoxime thus only warrant the conclusion that the experimental result agrees qualitatively with expectations.

The ozonization is carried out in a chloroform solution at -25 to -30°C . The solution of the ozonides is treated with a solution of hydroxylamine hydrochloride and soda in water. As primary aromatic scission products of the ozonides phthaldialdehyde and dimethylphthalaldehyde are formed; part of these dialdehydes is oxidized by the hydrogen peroxide, which is also formed, to the corresponding phthalaldehydic and phthalic acids. The remaining dialdehydes and the aldehydic acids react with hydroxylamine and yield various derivatives.

As primary aliphatic scission products of the ozonides are formed: dimethylglyoxal — a major part of which is oxidized to acetic acid, the remaining part being converted by hydroxylamine into dimethylglyoxime, methylglyoxal and glyoxal, which are also converted into dioximes.

The following compounds were isolated:

aromatic scission products	{	phthalic acid (35%), phthalimide (5 %), mono-oxime of phthalimide (10 %), dioxime of phthalimide (about 1 %), 4,5-dimethylphthalic acid, 4,5-dimethylphthalic acid imide.
aliphatic scission products	{	dimethylglyoxime (9 %), methylglyoxime (about 0.4 %), glyoxime (1.4 %), acetic acid (70–75 %).

The isolated compounds (except acetic acid) were identified with a synthetic sample by melting point and mixed melting point. The 4,5-dimethylphthalic acid imide was identified by the infra-red spectrum, which was identical with that of a synthetic sample. The yield figures placed between brackets have been calculated on the quantity of original dimethylnaphthalene. For some decomposition products the yield cannot be stated. The above figures represent minimum values, because a quantitative determination of the yields was impossible.

From the available data we conclude that the diozonide formation proceeds to the extent of about 90 % according to reaction A.

From the view point of the classical structural theory the experiments described in § 2 and § 3 warrant the following conclusion: the main ozonolysis products are formed by decomposition of diozonides, which may be formed from the ERLÉNMEYER–GRAEBE structure as well as from one of the ERDMANN structures. A slight quantity of by-product, methylglyoxal, is formed by decomposition of a pentozonide, which may be formed from one of the ERDMANN structures. The assumption that the naphthalene ring reacts mainly according to an ERLÉNMEYER–GRAEBE structure is therefore not in contradiction with our experiments.

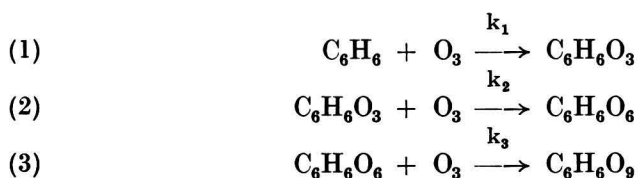
§ 4. *The mechanism of the ozonization according to the localization hypothesis*

KOORMAN and KETELAAR [10] are of opinion that the assumption that

the naphthalene molecule is converted into one of its valency structures, which subsequently reacts with ozone, must be rejected on energetic grounds. They justly observe that in the ozonization of benzene or naphthalene some consecutive reactions develop. First of all an ozone molecule will react to form a mono-ozonide. The mono-ozonide of benzene contains a non-aromatic ring system in which two double bonds occur; the mono-ozonide of naphthalene contains one double bond. These mono-ozonides will then rapidly react with ozone to form a triozonide or a diozonide.

This theory has been confirmed by measurements on the rate of the ozonization reaction of aromatic compounds, carried out in our laboratory by SIXMA [11] and some co-workers.

By representing the velocity constants of the three consecutive reactions by k_1 , k_2 and k_3



it follows from our measurements that the reaction velocity is determined by the slowest reaction, i.e.

$$\frac{d[\text{C}_6\text{H}_6]}{dt} = k_1 [\text{C}_6\text{H}_6] [\text{O}_3].$$

The value of k_1 at -31°C is 4.9×10^{-5} (m.mol $^{-1}$, liter, min. $^{-1}$).

Series of experiments, in which either the initial concentration of benzene, or that of ozone was varied, showed that the reaction is of the first order, both with respect to the benzene concentration and the ozone concentration.

We determined the value of k_1 at 6 temperatures ranging between -39.8°C and -25°C and calculated for the energy of activation: 12.4 ± 0.3 kcal/mol.

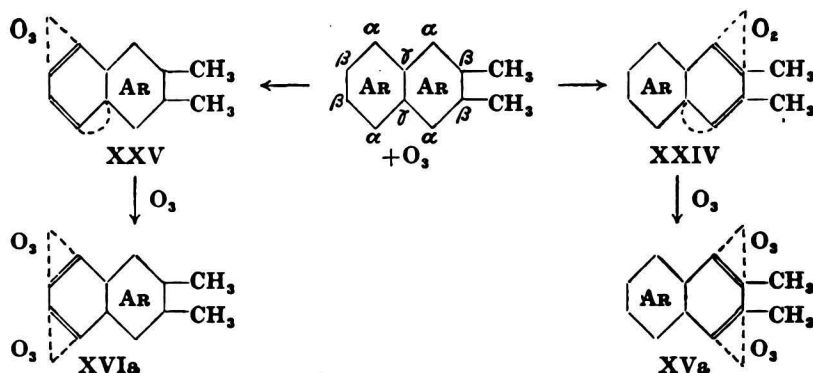
If the reacting benzene molecule is converted into a valency structure the reaction complex will, according to KOOYMAN and KETELAAR, consist of an ozone molecule and a hydrocarbon molecule with single and double bonds. This state cannot be attained until the total resonance energy has been taken up; this resonance energy thus forms part of the activation energy required for the reaction between ozone and benzene. The difference in activation energy of the ozonization of naphthalene and of benzene will be approximately the same as the difference in resonance energy of naphthalene and benzene, i.e. $75-39 = 36$ kcal/mol.

It might therefore be expected that naphthalene would react far more slowly with ozone than benzene. However, our measurements showed that at -30° naphthalene reacts about 10^4 times as rapidly as benzene. KOOYMAN and KETELAAR therefore developed a different mechanism,

based on the localization hypothesis [10]. They assume that in the reaction between an ozone molecule and the aromatic molecule the carbon bond, which is attacked by ozone, owing to localization of two π -electrons, is transformed into a polarized double bond, the other π -electrons tending to a state of minimum energy.

By starting from this assumption the authors deduce that in the case of naphthalene, localization of the 1,2-bond requires a smaller amount of energy than localization of the 2,3-bond, so that a reaction in which an α - β -bond is attacked, will show a far smaller energy of activation than a reaction in which a β - β -bond is attacked.

According to KOOYMAN and KETELAAR localization to an α - β -bond in 2,3-dimethylnaphthalene can take place in two ways:



By a further reaction with ozone, XXIV is converted into the diozonide (XVa) which, on being decomposed, yields phthalaldehyde and dimethylglyoxal; XXV is converted into the diozonide (XXVIa) from which dimethylphthalaldehyde and glyoxal are formed. XXVIa may yield two isomeric pentozonides, one of which (formula XXII in § 3), on being decomposed, yields glyoxal and methylglyoxal.

The view of KOOYMAN and KETELAAR that the α - β -bond in the ring system of naphthalene is more reactive than the β - β -bond leads to the same conclusions as the view that naphthalene and its derivatives react preferentially according to the ERLÉNMEYER-GRAEBE structure.

Contrary to the classical structural-chemical views of FIESER and FRIES, however, the theory of KETELAAR and KOOYMAN allows for the arguments and results of the theory of resonance.

As appears from our investigation, the methylglyoxal can only be formed from the pentozone (XXII); as we have shown that the formation of a pentozone proceeds far more slowly than that of a diozonide, it is clear that only a small quantity of methylglyoxal is formed.

§ 5. *The electrophilic mechanism of the ozonization*

Experiments started in our laboratory with SIXMA, KAMPSCHEIDT and BOER and which are being continued by SIXMA, showed that the influence

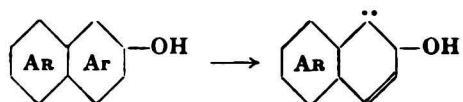
SIXMA [14] demonstrated by a calculation according to the molecular orbital method that localization of two π -electrons to an α -C-atom of the naphthalene ring requires less energy than localization to a β -C-atom. The calculated difference in localization energy for the α and β positions is of the same order as the difference in activation energy calculated from the bromination experiments by SUYVER and WIBAUT.

From this it follows therefore that an ozone molecule will react preferentially with an α -C-atom, the α - β -bond being polarized, for in this case the primary products formed contain an aromatic ring system. Formation of a primary product with polarization of the α - γ -bond is, on energetic grounds, less probable, as may be deduced from the localization theory of KOOYMAN and KETELAAR.

The ozonization of 2,3-dimethylnaphthalene can therefore be represented by the formulae on the preceding page. The primary products XXVI and XXVII will be stabilized to form the mono-ozonides XXVIII and XXIX, from which the diozonides XVa and XVIa are formed by the action of ozone.

Ultimately, the same diozonides are formed as according to the formulations given in § 3 and § 4.

The theory on the development of the monobromination of naphthalene suggested by WIBAUT and SIXMA also applies to the substitution in β -naphthol (see § 1). In this case too it may be assumed that the localization of two π -electrons occurs preferentially to an α -C-atom, so that the activated state of the α -naphthol molecule is represented by:



The reaction of β -naphthol with chlorine or with a diazotised amine allows of the same interpretation as the non-catalytic bromination of naphthalene.

The localization theory thus accounts for the experimental results formed in the ozonolysis of naphthalene and dimethylnaphthalene and for the substitution in β -naphthol and related phenomena. The results obtained by FIESER, FRIES, et. al. are therefore not in contradiction with the results of our investigations.

Summary

The action of ozone on naphthalene at -25°C to -40°C results in the formation of a diozonide, which continues to react slowly with ozone to form a pentozonide.

From 2,3-dimethylnaphthalene two isomeric diozonides are formed; the diozonide, in which the methylated six-membered ring has taken up two ozone molecules, is formed as main product. The other diozonide, in which

the non-methylated six-membered ring has taken up two ozone molecules, is formed as by-product.

The first stage in the action of ozone on the naphthalene ring system is the addition of one ozone molecule according to an electrophilic mechanism. The ozone reacts with an α -C-atom of one of the six-membered rings, an α - β -bond being polarized. The primary reaction product is stabilized to a mono-ozonide, which is rapidly converted into a diozonide.

The primary decomposition products formed by hydrolysis of the diozonide of naphthalene are phthaldialdehyde and glyoxal. In the case of dimethylnaphthalene the diozonide, the main product, is converted into phthaldialdehyde and dimethylglyoxal. From the diozonide formed as by-product, 4,5-dimethylphthalaldehyde and glyoxal are formed as primary decomposition products. A small part of this diozonide is converted into a pentozonide, from which by hydrolysis methylglyoxal is formed.

The theory on the mechanism of mono-ozonide formation developed by us accounts for the experimental data without being in contradiction with the theory of resonance.

From the viewpoint of the classical structural theory the result can be formulated by stating that naphthalene and dimethylnaphthalene, when acted upon by ozone, chiefly react according to the ERLLENMEYER-GRAEBE structure.

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Amsterdam, September 1950.

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