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REACTIONS OF OZONE WITH ALKENES

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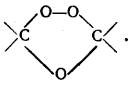
1. INTRODUCTION

Although the reaction of ozone with a carbon–carbon double bond has been known since 1855, when Schönbein was the first to accomplish the ozonisation of ethylene, a more or less clear idea of the nature of this reaction has been formulated only during the past 10–15 years. The products of ozonisation, which include, besides ozonides, α-substituted hydroperoxides, dimeric keto-peroxides, etc., occupy a prominent position in the chemistry of peroxy-compounds, owing to their ease of preparation and the possibility of converting them into aldehydes, alcohols, and other organic products. For many chemists, however, ozonisation has remained merely a means of determining the position of a double bond, and its value as a powerful synthetic tool is often underrated. The industrial application of ozonisation has recently been steadily increasing. Plant has already been operating during the past few years in which azelaic and nonanoic acids are manufactured by the ozonisation of oleic acid, and several other industrial methods have been developed[1-11]. Recent advances in the development of new applications of ozonisation and in improving the manufacture of ozone indicate that this reaction will become increasingly important in industry.

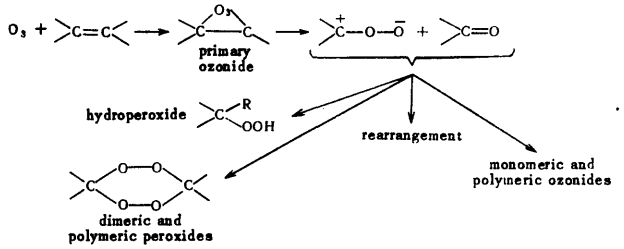
No review on ozonisation or the properties of the reaction products has been published in the Soviet literature. The foreign literature contains fundamental papers on this question[12-18], which discuss the preparation and chemical transformations undergone by ozonides of various structures. The present Reviewers have set themselves a more modest aim: this survey is concerned mainly with the synthesis of ozonides of aliphatic alkenes, a field in which research is being undertaken for the purpose of the practical exploitation of the ozonisation of alkenes for the production chiefly of higher aliphatic aldehydes, acids, and alcohols.

2. INTERACTION OF OZONE WITH ALKENES

In the early work on ozonisation, among which that of Harries[19-21] occupies an important place, many unsaturated compounds were subjected to this reaction, but no definite conclusions were reached concerning the structure of the products or the mechanism of the reaction. In 1925 Staudinger[22] suggested for an ozonide a formula comprising a five-membered peroxy–ether ring

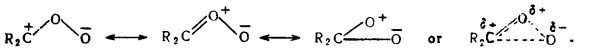


This structure was subsequently confirmed by Rieche et al.[23,24] by an alternative synthesis of the ozonide of but-2-ene. However, ozonides do not constitute the sole products of ozonisation. A more or less general mechanism of ozonisation, covering interaction with various unsaturated compounds under various reaction conditions, was suggested by Criegee and his coworkers[25-39]. This mechanism provides an explanation of most of the experimental facts known at the present time. Criegee's scheme can be represented in general as follows



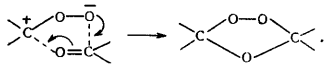
A key position in this scheme is occupied by the zwitterion, the life of which is taken to be sufficient for it to be regarded as a true intermediate product.

In most cases the primary ozonide, formed as a result of bipolar 1,3-addition of ozone to the alkene, immediately breaks down with fission of the O–O and C–C bonds by a concerted mechanism. The zwitterion is formed at one end or the other of the former double bond depending on which carbon atom receives the electron pair of the remaining C–C bond. The resulting zwitterion is stabilised by conjugation:



Stabilisation of the zwitterion can be effected in four main ways, by — (1) interaction with the simultaneously formed carbonyl compound, with formation of monomeric or polymeric ozonides, (2) dimerisation or polymerisation with formation of dimeric or polymeric peroxides respectively, (3) interaction with a proton-donating solvent with formation of hydroperoxides, or (4) rearrangement — the way in which it occurs being determined by the structure of the initial alkene, by the solvent, and to a less extent by the reaction conditions. In most cases the zwitterion reacts in more than one way simultaneously.

The first mode of stabilisation — bipolar addition of the 1,3-zwitterion to a carbonyl group[38] — usually takes place when the simultaneously formed carbonyl compound is an aldehyde:



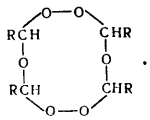
Ketones do not usually react with the zwitterion by the above 1,3-bipolar scheme leading to formation of an ozonide.

It has been noticed that most alkenes on ozonisation in an inert solvent give their "own" ozonides: i.e. a definite "cage effect" is operative. Thus the ozonisation of a mixture of oct-4-ene and hex-3-ene yields only the ozonides of

these alkenes, and the ozonisation of hept-3-ene gives only the ozonide of hept-3-ene [12]. However, this is not an absolute effect. Riezebos et al. [39] have reported the isolation of three pairs of stereoisomeric ozonides from the products of the ozonisation of methyl oleate. Loan et al. [40], while confirming the presence of a cage effect, showed, with the ozonisation of pent-2-ene as example, that some of the zwitterions jump out of the cage and enter into "extracellular" reactions even in highly dilute solution in an inert solvent. On the other hand, part of the ozonide reacts inside the cell even in the presence of excess of aldehydes, which are known to destroy the cage effect [28]. With increase in the concentration of alkene in the solvent, the relative proportions of "own" and "cross" ozonides approach the statistical values [40].

Criegee and his coworkers prepared several monomeric ozonides, purified them by distillation or recrystallisation, and determined their physicochemical constants [31]. These workers showed that only ozonides of low-molecular-weight alkenes are explosive: the ozonides of butene and higher homologues are quite stable liquids or solids, which can be subjected to distillation, crystallisation, and other operations. In all twenty-two monomeric ozonides were obtained in this work, including those of hex-1-ene, hex-2-ene, hex-3-ene, oct-3-ene, styrene, stilbene, etc. The preparation of ozonides of cyclopentene and cyclohexene had previously been reported [27]. The present Reviewers have isolated ozonides of hex-1-ene, hept-1-ene, and oct-1-ene, purified them by treatment with sodium bisulphite and fractional distillation on a column, and shown by infrared spectroscopy that the products were not contaminated with carbonyl compounds [41].

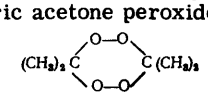
In the ozonisation of alkenes which yield monomeric ozonides as the main products, quite considerable quantities of compounds of high molecular weight are formed. Both Harries [19] and later investigators [14] have regarded these products as dimeric ozonides



Rieche et al. [24] obtained a product having this structure on synthesising the ozonide of but-2-ene from acetaldehyde and hydrogen peroxide.

The present Reviewers [42], on ozonising hex-1-ene, obtained, together with the monomeric ozonide, products of the addition to the zwitterion of two and three molecules of formaldehyde. The same work showed that a dimeric ozonide is not the main component of the residue remaining after the monomeric ozonide has been distilled off. The residue in the flask probably consists mainly of linear polymers containing a terminal hydroperoxy-group, the presence of which was confirmed by infrared spectra.

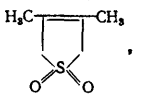
Another mode of stabilisation of the zwitterion is by its dimerisation or polymerisation. These reactions occur mainly when the carbonyl compound, formed together with the zwitterion on breakdown of the primary ozonide, is a ketone. Thus Criegee [27], on ozonising 2,3-dimethylbut-2-ene, obtained dimeric acetone peroxide



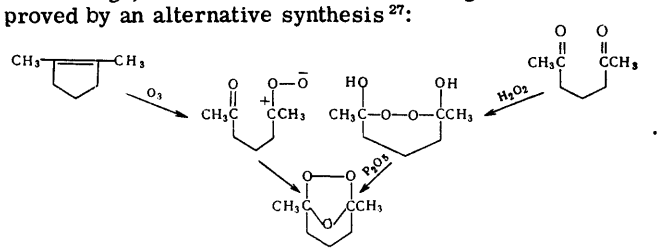
together with an extremely explosive substance, which he described as a polymer of the zwitterion $(CH_3)_2C^+-O-O^-$. Examples of other compounds which give a ketone and dimeric or polymeric peroxides on ozonisation are tetraphenylethylene [43], 1-8-octahydronaphthalene [25], bi(cyclohexylidene) [27], and bi(cyclopentylidene) [27]. Dimeric keto-peroxides can be obtained also by treating the corresponding ketones with persulphuric acid or hydrogen peroxide [16]. Polymeric peroxides have not yet been isolated as products of definite structure. They are usually described as explosive, viscous oils or amorphous solids [14,27]. Those of high molecular weight are probably linear polymers of the zwitterion $\rangle C^+-O-O^-$.

Before the publication of Criegee's work, many authors spoke of "perozonides" and "oxozonides" [12,14,20]. Most of these compounds containing more oxygen than the ozonide are probably dimeric or polymeric peroxides.

There are at least two exceptions to the rule that ozonides are not formed from compounds which give a ketone together with the zwitterion on ozonisation. The first exception is provided by cycloalkenes in which the double bond forms part of a five-membered (sometimes four-membered) ring, and the second by ketones containing an activated keto-group. Compounds of the first type include 1,2-dimethylcyclopentene [26,27,31], the cyclic sulphone [27]



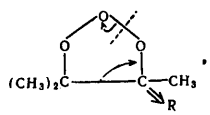
maleimide [31], certain derivatives of indene, and steroids. The ozonides of unsaturated five-membered rings are usually very stable. Thus the ozonide of the above sulphone melts at 154°, and is stable to heating (at 100° for 5 h). The driving force causing intramolecular cyclisation of zwitterions formed in the ozonisation of unsaturated rings is probably the formation of classical five- to seven-membered rings (together with five-membered trioxolan rings). Cyclohexene and cycloheptene derivatives, which would have given seven- to nine-membered rings on intramolecular cyclisation, yield mainly polymeric ozonides and peroxides on ozonisation [26,27,31]. In the case of five-membered rings, the structure of the resulting ozonides was proved by an alternative synthesis [27]:



In the ozonisation of systems containing unsaturated five-membered rings, the yield of monomeric ozonides is higher if the hydrogen atoms attached to both carbon atoms linked by the double bond have been substituted. The absence of substituents in the zwitterion and (or) the carbonyl group at the ends of the decomposition product obviously permits intermolecular reaction to compete successfully with intramolecular cyclisation. An exception is the sulphone of 5,5-dimethylhexa-1,3-diene, which gives an 85% yield of the ozonide [27]. Ozonides of this type can be obtained also by the photoactivated autoxidation of certain furans (2-methyl- and 2,5-dimethyl-furan) [44] and also dimethylisobenzofuran [45].

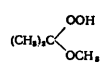
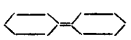
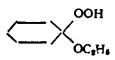
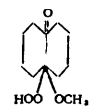
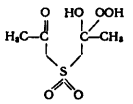
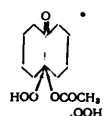
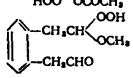
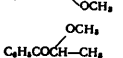
The second exception to the rule that ozonides are formed only from a zwitterion and an aldehyde is provided by the ozonisation of alkenes containing substituents possessing a considerable negative inductive effect. Criegee

et al.[34] obtained monomeric ozonides from *cis*- and *trans*-$BrCH_2C(CH_3):C(CH_3)CH_2Br$ (I), $(CH_3)_2C:C(CH_3)COOCH_3$, and $(CH_3)_2C:C(CH_3)CHO$ (II). This shows that activated ketones — bromoacetone, methyl pyruvate, and methylglyoxal — react like aldehydes with the zwitterion. Both *cis*- and *trans*-isomers of (I) give mixtures of the corresponding liquid *cis*-ozonide and solid *trans*-ozonide (dipole moments 2.45 and 2.25 D respectively). These results were obtained when (I) was ozonised in pentane, whereas when dichloromethane is used as solvent, *cis*-(I) gives bromoacetone in 90% yield together with a peroxide (presumably a dimeric peroxide of bromoacetone). The ozonide obtained by the ozonisation of (II) is the ozonide not of (II) but of 4-methylpent-3-en-2-one. The formation of the same ozonide by these two compounds is explained by the fact that the methylglyoxal obtained in the first stage reacts in both cases not at the ketonic but at the aldehyde group. The results clearly show the influence of inductive effects on the breakdown of the primary ozonide: in all cases the electron pair of the C–C bond goes to the atom having the more electronegative substituent (the alternative in which an ozonide is formed from acetone, of course, is not included):



where R = CH_2Br, $COCH_3$, CHO. However, the formation of small quantities of a mixed anhydride of formic and acetic acids, which can result only from rearrangement of the zwitterion $CH_3COCH^+OO^-$, shows that migration of the electron pair to the other carbon atom does also take place.

TABLE 1. Products of ozonisation in solvents containing an active hydrogen atom.

No.	Alkene	Solvent	Product	Yield, %	Ref.
1	$(CH_3)_2C=C(CH_3)_2$	CH_3OH		77	27
2		$CCl_4 + C_2H_5OH$		68	27
3		CH_3OH		88	25
4		acetone + water		57	27
5		acetone + CH_3COOH		—	25
6		CH_3OH		42	46
7	$C_6H_5COCH=CHCOC_6H_5$	acetone + CH_3OH		60	47
8	$C_6H_5COCH=CCOC_6H_5$ CH_3	acetone + CH_3OH		74	47

* Unstable — isolated as benzoylperoxy-derivative.

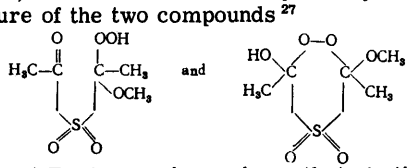
All workers regard the products obtained by the ozonisation of alkenes in solvents containing an active hydrogen atom as α-substituted hydroperoxides



where R′ is the residue of an alcohol, acid, etc. Table 1 lists several alkoxy-, hydroxy-, and acyloxy-alkyl hydroperoxides obtained by ozonolysis in "active" solvents. Many of these substances are perfectly stable, and possess high melting points (the hydroperoxide No. 4 melts at 94–95°). Hydroperoxides obtained by the ozonolysis of cyclic molecules do not preserve a simple hydroperoxide form if an aldo-group is present at the other end of the chain[48]. This is explained by interaction between the hydroperoxy- and aldo-groups with formation of peroxyhemiacetals and peroxyacetals[11].

The examples in Table 1 relate to alkenes having substituents adjacent to the double bond. Murai et al.[49] have recently subjected an unbranched-chain α-alkene, oct-1-ene, to ozonisation in ethanol. They obtained a product which, from its molecular weight and content of available oxygen, they regarded as 1-ethoxy-n-heptyl hydroperoxide.

Intramolecular reactions occur during the ozonolysis of phenanthrene[50], naphthalene[51], and indene[52] in methanol or ethanol. A tendency to cyclisation is present even when a keto-group is located at the other end of the chain. The product of the ozonolysis of the cyclic sulphone of 2,3-dimethylbuta-1,3-diene in methanol is probably an equilibrium mixture of the two compounds[27]



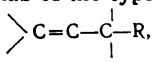
The present Reviewers have shown that, in the ozonisation of alk-1-enes in alcohols, the mode of stabilisation of the zwitterion depends on the relative proportions of alcohol and alkene. When hex-1-ene undergoes ozonisation with a hexene–ethanol molar ratio exceeding 1:10, formation of the hydroperoxide is accompanied by that of hex-1-ene ozonide[53].

Rearrangements, which together with epoxidation constitute a group of so-called "anomalous cases of ozonisation", are encountered far less frequently than the three types of reaction discussed above.

The ozonisation of alkenes in which groups which can cause steric hindrance are present on one of the carbon atoms joined by the double bond often results in epoxides or products of their rearrangement containing the same number of carbon atoms as the original alkene. Examples of such compounds are 1-mesityl-1-phenylethylene and 3,3,5-trimethyl-2-t-butylhex-1-ene, which on ozonisation give 2-mesityl-2-phenylvinyl alcohol[54] and an epoxide[55] respectively. Criegee[32] repeated the ozonisation of the first of these unsaturated compounds in the presence of triethylamine (to prevent rearrangement of the epoxide under the influence of the acids formed during the reaction), and obtained an epoxide which in the presence of acids readily rearranged into the enol obtained by Fuson[54]. Other cases are known of the formation of oxides of alkenes on ozonisation[56,57].

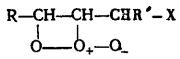
In many cases products have been isolated which contained fewer carbon atoms than would have been expected on the usual ozonolysis of the double bond. Formation of

such products has been observed most frequently in the ozonisation of compounds of the type

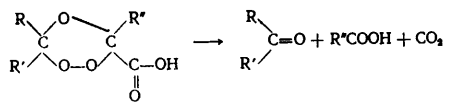


where R represents various substituents usually containing O, N, or S.

Young[58] and Leffler[62] ozonised compounds of the type RCH:CHCHR'–X (where X = Hal, OH, NR_2'', OR''', or OCOR'''') in inert solvents, and showed, from the results of a quantitative determination of the acids, that the usual products of ozonolysis are formed when X = Cl, Br, or $OCOCH_3$. They arranged the substituents X, according to their influence on the isolation of anomalous products, in the sequence Cl, Br, or $OCOCH_3 < p\text{-}OC_6H_4NO_2 < OC_6H_5 <$ $< OH < OCH_2CH_3 < N(C_2H_5)_2$. Examples of the compounds investigated by these workers are but-3-en-2-ol, which on ozonisation gives, together with formic acid (yield 75%), acetic acid (25%) (instead of lactic acid); and also CH_3CH: $:CHCH_2N(C_2H_5)_2$, giving on ozonisation, together with acetic acid (46%), formic acid (54%) (instead of diethylaminoacetic acid). The anomalous products were shown[58] to be formed neither as a result of allylic rearrangement of the initial alkene nor as a result of an oxidation process. All cases of the formation of anomalous products in large quantities involved spontaneous decomposition of peroxy-products of ozonisation with the evolution of carbon monoxide. The results were explained by rearrangement of Staudinger's "molozonide"

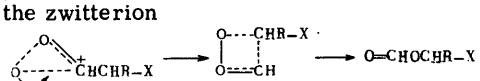


Similar results have been obtained in the ozonisation of CH_3CH:CHCOOH, CH_3CH:CHCHO, CH_3CH:$CHCOCH_2CH_3$, and several cyclic systems[59]. Barton and Seoane suggested[59] the mechanism

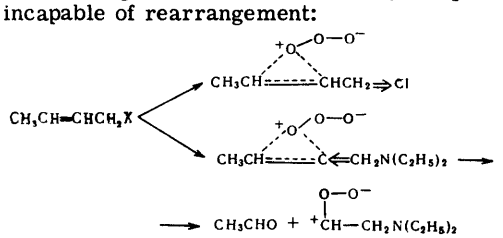


to explain the anomalous ozonolysis observed with $\alpha\beta$-unsaturated acids. This mechanism does not explain the formation of carbon monoxide.

Bailey[14] puts forward a mechanism involving rearrangement of the zwitterion



to explain anomalous ozonolysis. He interprets the increase in ability of the group X to promote rearrangement as its electronegativity diminishes in terms of the influence of inductive effects on the breakdown of the π-complex, the positive I-effect of the diethylamino-group favouring formation of a zwitterion containing X, i.e. of a zwitterion capable of rearrangement, whereas the high $-I$-effect of a halogen or $OCOCH_3$ contributes to formation of a carbonyl compound containing X and a zwitterion of type $R_2^+COO^-$, which is incapable of rearrangement:



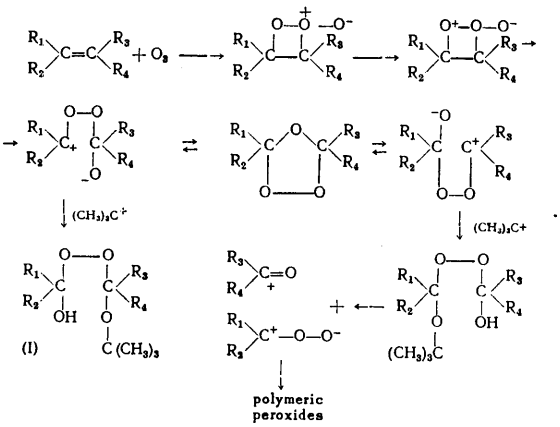
However, an anomalous course of the reaction was observed in the ozonisation of several 2-substituted naphthaquinones, which could not be explained in terms of differences between the inductive effects of the substituents[60]. Furthermore, if it is assumed that anomalous ozonolysis is caused by rearrangement at the zwitterion stage, *cis*-2-methyl-1,4-diphenylbut-2-ene-1,4-dione and 2-methylnaphthaquinone should give similar products, whereas actually the ozonolysis of these two compounds goes in opposite directions. Hence Bernatek et al.[60] have assumed that the course of anomalous ozonolysis is determined, not at the zwitterion stage, but at the stage of the primary ozonide, to which they attribute a structure in which the π-electrons are preserved (see below).

Small quantities of anomalous products are formed also in the ozonisation of "normal" alkenes. Thus the ozonolysis of dodec-6-ene yields 2–8% of valeric acid and 0.8–1.2% of butyric acid, that of cyclohexene gives 4.7% of glutaric acid and 1.8% of succinic acid[61], etc. These products are most probably formed not only as a result of rearrangement but also by the oxidation of "normal" products of ozonolysis. It is known[61,62] that the oxidation of aldehydes may yield products containing a smaller number of carbon atoms than the original aldehyde.

It is difficult to explain the formation of carbon dioxide, methane, and hydrogen in the ozonolysis of oleic acid[24], of methane from but-2-ene, of hydrogen from but-1-ene[63], and several other results.

Most anomalous products of ozonolysis are formed in inert solvents. In many cases the anomalous ozonolysis can be prevented by conducting it in methanol and then reducing the products[64]. However, the alkoxylated hydroperoxides which are formed sometimes also undergo rearrangement[30]. Anomalous ozonolysis has been observed also with the compounds C_6H_5COCR:$CHCOC_6H_5$, which give benzoic acid and methyl formate on ozonisation in methanol followed by slight heating or decomposition with alkali in the cold[47].

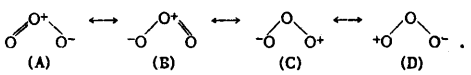
A mechanism differing somewhat from that of Criegee was suggested by Milas for the formation of peroxy-products of ozonolysis. According to this, the ozonide (the 1,2,4-trioxolan) is an intermediate in the formation of all ozonisation products. Milas postulates the existence of a zwitterion of the type $\diagdown C^+-O-O^-$, but assigns to it a subordinate role as intermediate in the formation of polymeric impurities. The main evidence of Milas' mechanism is the formation of the compound (I) on the ozonisation of alkenes in the presence of the trimethylcarbonium ion (i.e. in t-butyl alcohol and concentrated sulphuric acid)[65]:



In a later paper Milas uses the same mechanism to explain the formation of polymeric peroxides in the ozonisation of 2,3-dimethylbut-2-ene in pentane[66]. This mechanism, even if it is valid for the above cases, undoubtedly has a narrower range of application than Criegee's mechanism.

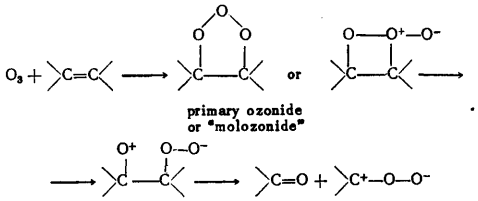
The most complex problem in the mechanism of ozonisation is the nature of the initial attack by ozone on the double bond and the structure of the primary products. This is due to the high speed of the initial reactions, which make a kinetic study extraordinarily difficult, and also the extreme instability of the initial products.

The structure of the ozone molecule is of fundamental importance to an explanation of the nature of the initial attack. Both bonds in ozone are 1.278 ± 0.002 Å long, with an angle of 116° ± 3° between them. The molecule is not paramagnetic; perhaps it is diamagnetic in the gaseous state. On the basis of these data it is represented by the following set of structures[67]



The electronic structure of the ozone molecule is such[67] that the central oxygen atom has three hybrid sp^2-orbitals lying in the same plane and one p-orbital perpendicular to this plane. Two of the three hybrid orbitals form σ-bonds with the terminal atoms, and the p-orbital forms a π-bond with one of the terminal atoms. The electrons forming this bond are delocalised. The third hybrid orbital is directed along the axis of symmetry of the molecule, and has an unshared pair of electrons. The surprisingly low dipole moment of the ozone molecule (0.56 ± 0.05 D) is explained by the fact that the high dipole moment of the third hybrid orbital operates in the opposite direction to the dipole moment of the canonical structures (A) and (B).

The addition of ozone to a double bond is usually supposed to proceed in the sequence

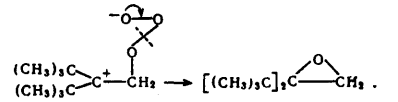


Criegee and Schröder[33] first isolated the primary ozonide of *trans*-2,2,5,5-tetramethylhex-3-ene, measured its heat of rearrangement into the usual ozonide (38.9 kcal × × mole^{-1}), and examined the reactions of this product with several substances. Reduction with sodium in liquid ammonia gave an αβ-diol. Ozonisation of the *cis*-tetramethylhexene under the same conditions did not yield a primary ozonide.

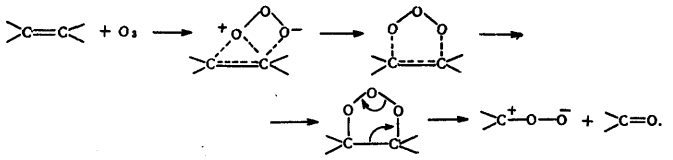
Later Schröder[68] and Greenwood[69] showed the formation of primary ozonides from *trans*-alkenes, and its absence with the *cis*-isomers, to be a general phenomenon. It was also established that the ozonisation of *cis*-2,2,5,5-tetramethylhex-3-ene yields *cis*- and *trans*-ozonides, whereas that of its *trans*-isomer gives predominantly the *trans*--ozonide[68].

Bailey et al.[70] examined the products of the ozonisation of monosubstituted derivatives of 1,4-diphenylbut-2-ene--1,4-dione with the aim of studying the mechanism of the initial attack by ozone on the double bond. The results obtained (i.e. the way in which the primary product decomposed, as a function of the substituent) pointed to none of the three schemes suggested previously — two-stage addition in conformity with the Markovnikov rule with formation of a four-membered ring (mode of decomposition determined by mesomeric effect of substituent), four-centre attack with formation of a five-membered ring (direction of decomposition determined by inductive effect of substituent), or a π-complex mechanism (the more stable of the two possible zwitterions being formed) — so that Bailey concluded that the type of attack varies with the nature of the alkene, and he listed five possible types of attack.

1. Electrophilic attack on a nucleophilic atom at the double bond, with formation of a σ-complex. This type of attack occurs, in Bailey's opinion, when marked steric hindrance is present at one end of the double bond, and it results in the formation of oxides of the alkenes:



2. Electrophilic attack on the double bond with formation of a π-complex. This type of attack takes place in the ozonisation of most unsaturated compounds†:



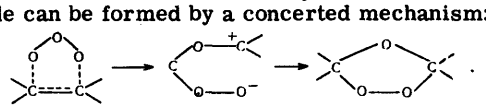
This mechanism enables most of the observed cases of ozonolysis to be explained in terms of the inductive effects of the substituents in relation to the five-membered ring of the primary ozonide. An exception is provided by *cis*- and *trans*-1,2,4-triphenylbut-2-ene-1,4-dione, whose ozonides break down in the opposite direction to that determined by the -*I*-effect of the phenyl group. In this case Bailey assumes partial maintenance of sp^2-hybridisation in the intermediate complex, and subsequent breakdown of the latter into a zwitterion by a concerted mechanism, the direction of which is determined by the mesomeric effect (+*M*) of the phenyl group.

3. Four-centre attack on the double bond with formation of a five-membered ring, which then breaks down as in mechanism 2.

4. Nucleophilic attack on an electrophilic atom.

5. Radical attack on certain saturated groupings (observed in the oxidising action of ozone).

In inert solvents and with not very stable zwitterions, an ozonide can be formed by a concerted mechanism:

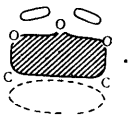


Bailey explains the formation of a primary ozonide from *trans*-2,2,5,5-tetramethylhex-3-ene, and its absence (together with a high yield of the usual ozonide) on ozonisation of the *cis*-isomer, by competition between this mechanism and the usual Criegee mechanism, such competition being governed by steric hindrance.

† In earlier papers Bailey[71] had put forward the hypothesis that the π-complex was converted into a zwitterion and a carbonyl compound without a stage involving formation of a primary ozonide.

However, the paper by Bernatek et al.[60] already mentioned gives data on the effect of the substituent in the anomalous ozonolysis of a substituted naphthaquinone which do not fit into Bailey's scheme: i.e. no correlation is observed with either the inductive or the mesomeric effects of the substituents (Table 2). From this it was concluded that the direction of ozonolysis is determined by polarisability effects at the primary ozonide stage, i.e. that the primary ozonide preserves the sp^2-hybridisation throughout its existence.

By analogy with the structure proposed by Walsh[72] for oxiran, these workers[60] assign to the primary ozonide a structure in which the p_y- and p_z-orbitals of the oxygen atoms (each containing one electron) are located in the plane of the ring, while the p_x-orbitals are perpendicular to the ring and contain two electrons. The two trigonally hybridised carbon atoms each contain one sp^2- and one p_z-orbital in the plane of the ring, together with two sp^2--orbitals above and below this plane. Overlapping between the sp^2-clouds of the carbon atoms and the p_y-clouds of the oxygen atom creates a delocalised electron cloud, which is responsible for the polarisability of the molecule. In the molecular-orbital treatment the structure of the primary ozonide has the appearance



The presence of six electrons in the delocalised orbital supports the hypothesis that the primary ozonide possesses considerable capacity for conjugation. On this hypothesis the authors derived the parameter Δ (the "absolute substituent constant"), which relates to the carbon atom of the double bond which has the largest total substituent constant:

$$\Delta_1 = |\Sigma\sigma C_1| - |\Sigma\sigma C_2| \text{ when } |\Sigma\sigma C_1| > |\Sigma\sigma C_2|$$
$$\Delta_2 = |\Sigma\sigma C_2| - |\Sigma\sigma C_1| \text{ when } |\Sigma\sigma C_2| > |\Sigma\sigma C_1|,$$

where $\Sigma\sigma C_1$ and $\Sigma\sigma C_2$ represent the sums of the substituent constants σ in the Hammett equation at one of the carbon atoms. In the case of 2-substituted naphthaquinones a satisfactory correlation was obtained between the Δi and the yield of *o*-glyoxyloylbenzoic acid.

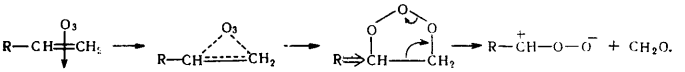
All ozonides contain a planar five-membered ring, and can therefore exist as *cis*- and *trans*-isomers. The existence of *cis*- and *trans*-ozonides was first detected by Schröder[68]. Privett and Nickell[73,74] isolated by thin-layer chromatography *cis*- and *trans*-ozonides of methyl oleate, and identified them from their infrared spectra. Riezebos et al.[39] isolated all six possible ozonides — *cis*- and *trans*-$CH_3[CH_2]_7CHO_3CH[CH_2]_7COOCH_3$, *cis*- and *trans*--$(CH_3[CH_2]_7CH)_2O_3$, and *cis*- and *trans*-$(CH_3OCO[CH_2]_7.$ $.CH)_2O_3$ — from the products of ozonisation. The products were characterised by their infrared and nuclear magnetic resonance spectra and by paper chromatography of their decomposition products (aldehydes and aldo-esters). The relative proportions of the ozonides depend on the temperature of ozonisation and the concentration of alkene in the solvent (petroleum ether). With a 10% concentration at 10° the distribution of all three above types of ozonides approximates to the statistical proportions of 2 : 1 : 1, but with a 0.5% concentration mainly the "proper" ozonide of methyl oleate is formed, the quantity of "cross" ozonides being small.

TABLE 2. Effect of substituent on yield of *o*-glyoxyloylbenzoic acid in the anomalous ozonolysis of 2-substituted 1,4-naphthaquinones.

Substituent	Yield, %	Substituent	Yield, %
—OH	90.4	—NHCOCH$_3$	13.8
—Cl	78.4	—O$^-$(OH + pyridine)	9.7
—C$_6$H$_5$	71.8	—NH$_2$	4.6
—OCOCH$_3$	71.3	—OCH$_3$	3.9
—N(CH$_3$)$_2$	21.0		

The formation of "cross" ozonides in the ozonolysis of methyl oleate brings us back to the question of the role of the "cage" of solvent molecules in the interaction of the zwitterion with the aldehyde. Escape of the zwitterion from the "cage" is fairly widespread in ozonisation. Loan et al.[40] ozonised pent-2-ene in the absence of solvent at -70°, and obtained a mixture of the ozonides of pent-2-ene, but-2-ene, and hex-3-ene in proportions close to random (2 : 1 : 1). When the initial ozonide was diluted with pentane, the yields of "cross" ozonides diminished. These workers observed that reaction takes place in the "cage" even in the presence of excess of a "foreign" aldehyde. From the relative proportions of the ozonides formed in this case it was assumed that 9.5% of the product recombines in the "cage", 51% yields the free zwitterion $CH_3CH^+OO^-$, and 39.5% gives the free zwitterion $CH_3CH_2CH^+OO^-$.

The experimental facts reported above and their interpretation permits us to make the following hypotheses concerning the course of the ozonisation of alk-1-enes of normal structure. On the basis of a scheme involving a π-complex passing into a molozonide five-membered ring, which is applicable to most alkenes, the direction of breakdown of the primary ozonide should be determined by the inductive effects of the substituents adjacent to the double bond. Since the distribution of inductive effects in this case is obvious — zero effect of hydrogen atoms and a positive inductive effect of an alkyl substituent — ozonisation of an alk-1-ene should involve formation mainly of an alkyl-substituted zwitterion and formaldehyde:



When the reaction is conducted in an inert solvent, the zwitterion reacts with the formaldehyde — the most reactive of the unsubstituted aldehydes — to form a monomeric ozonide. Some of the zwitterions may escape from the cage, but in view of the preferential occurrence of breakdown by the above mechanism, opportunities for the formation of "cross" ozonides are very limited. Ozonisation in active solvents — alcohols, carboxylic acids, etc. — should yield mainly the corresponding derivatives of the zwitterion $\rangle CH^+OO^-$ and formaldehyde.

3. PROPERTIES OF OZONISATION PRODUCTS

It follows from the discussion in Section 2 that the main products of ozonisation are monomeric and polymeric ozonides, dimeric and polymeric peroxides, and also products of ozonisation — α-substituted hydroperoxides — in active solvents. Very little is known about the chemical properties of the ozonisation products. Ozonides have been somewhat more fully studied, but of dimeric and polymeric peroxides it is known only that in most cases they are explosive, viscous oils. Almost nothing is known also of the structure of the polymeric ozonides.

Since the first application of ozonisation was to determine the position of the double bond in unsaturated compounds, investigation of the products of ozonisation began with a study of methods for their conversion into stable products — acids, aldehydes, alcohols, etc. — which could be identified. For the most part these methods consisted merely in oxidation, reduction, thermal decomposition, and hydrolysis. Many of them were at one time patented, but only a few of them found industrial application.

Ozonolysis followed by oxidation is most often employed as a method for determining the position of a double bond. Asinger's method[75] — ozonisation in a hot suspension of silver oxide in the solvent — is generally used. It converts alkenes quantitatively into acids. Asinger has recently supplemented this method with gas-chromatographic analysis of the acids as their methyl esters[76]. Very often the decomposition products are oxidised with oxygen, while ozone or a metal salt is used as initiator. The firm Emery Industries Inc. uses this method to produce azelaic and nonanoic acids on an industrial scale from oleic acid of vegetable origin[1]. The very promising method of Otsuki and Funahashi[77] consists in ozonising oleonitrile and then subjecting the product to oxidising decomposition with formation of the 8-cyano-octanoic acid, which was then reduced to 9-aminononanoic acid. Examples of the oxidative ozonolysis of other compounds are given in Table 3. Several patents have been taken out on oxidative ozonisation[7-9]. Besides the oxidising agents which have been listed, use is made also of hydrogen peroxide as an aqueous solution or mixed with acetic, sulphuric, or formic acid. These methods have been described in the reviews by Long[12] and by Bailey[14]. Oxidative decomposition is sometimes accompanied by rearrangements[61].

Reduction of the ozonisation products is, perhaps, the method showing the greatest industrial promise. Existing methods of reduction can be divided into two groups — reduction to aldehydes and ketones, and reduction to alcohols.

For preparative purposes use is made most often of reduction with sodium or potassium iodide, reduction with zinc or magnesium in the presence of water or acetic acid[12,14], and also catalytic reduction on palladium or other catalyst[28,78,79]. Other reducing agents are sodium bisulphite, sulphur dioxide, tin(II) chloride, and formaldehyde. Examples of these reactions are given in Table 4.

Reduction of the ozonides with hydrogen on a Lindlar catalyst[79] at 0°, followed by gas-chromatographic analysis of the resulting aldehydes, is sometimes used for determining the position of a double bond.

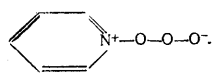
TABLE 3. Oxidative decomposition of products of ozonolysis.

Compound ozonised	Solvent	Product (acid)	Method of decomposition	Yield, %	Ref.
Cyclohexene	CH_3OH	adipic	$O_2 - O_3$, HCOOH	73	80
»	»	»	ditto	85	48
»	CH_3COOH	»	CH_3COOH	86	81
Oct-1-ene	CH_2Cl_2	heptanoic	$O_2 - O_3$, CH_3COOH	83	13
Dodec-1-ene	CH_3COOH	undecanoic	$O_2 - O_3$, CH_3COOH	77	13
»	pentane	»	Ag_2O + NaOH	93	75
Tridec-1-ene	$CHCl_3$	lauric	ditto	94	75
Naphthalene	CH_3OH	phthalic	$O_2 - O_3$, HCOOH	88	51
cis-Octadec-9-enylamine	CH_2Cl_2	9-aminononanoic	air, Mn catalyst, HCl	25	77

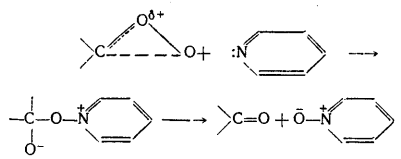
TABLE 4. Reduction of ozonisation products.

Compound ozonised	Product	Solvent	Method of reduction	Yield, %	Ref.
Cyclohexene	adipaldehyde	CH_3OH	catalytic	54	79
1,2-Dimethyl-cyclopentene	heptane-2,6-dione	CCl_4	»	74	31
Stilbene	benzaldehyde	$CH_3OH + CH_2Cl_2$	steam	93	13
Styrene	»	ditto	»	37	13
Phenanthrene	biphenyl-2,2′-dial	CH_3OH	NaI	84	82
Camphene	camphenilone	CH_3OH	NaI	75	30

The reduction of ozonisation products to aldehydes and ketones is used in the preparation of piperonal from isosafrole and of vanillin from isoeugenol[83]. The reducing agents tried in this work were $NaHSO_3$, $FeSO_4$, $K_4[Fe(CN)_6]$, $SnCl_2 + HCl$, Sn + HCl, Zn + CH_3COOH, $(NH_4)_2Fe(SO_4)_2$, KI + CH_3COOH, H_2O + Zn, $AgNO_3$, quinol, pyridine, and piperidine. An aldehyde (3-oxobisnorchol-4-en-22-al) is formed also in the ozonolysis of ergosta-4,22-dien-3-one[84]. The role of added pyridine in these reactions is very interesting. Pyridine considerably increases the yield of piperonal and of the above hormone. The direction of the reaction on ozonisation in pyridine medium is probably a result of complex formation between pyridine or pyridine oxide (formed on ozonisation) and ozone[85]. This diminishes the electrophilic character of the ozone molecule, which can then react only with the most electron-donor double bond:



In the presence of pyridine the above steroid, as well as isosafrole, yields two moles of aldehyde, whereas in the absence of pyridine only one mole of aldehyde is formed. This is probably explained by the pyridine attacking the zwitterion with formation of pyridine oxide and the aldehyde:



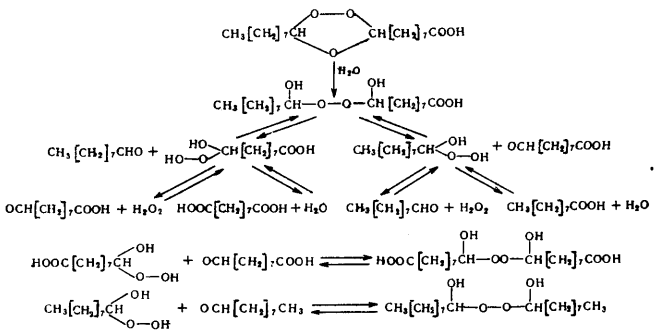
Catalytic reduction has been used for the production of 9-aminononanoic acid. In one case the products of the ozonolysis of oleic acid were reduced in two stages, the second stage of reduction being conducted in the presence of ammonia or hydroxylamine[10,86]. Recently Pollart and Miller[87] have proposed a single-stage method of reduction without preliminary isolation of the carbonyl compounds. Hexamethylenediamine has been obtained similarly by the ozonolysis of cyclohexene. 9-Aminononanoic acid and hexamethylenediamine are starting materials for the manufacture of 9-nylon and 6,6-nylon respectively.

Treatment of the products of ozonisation with an acid solution of 2,4-dinitrophenylhydrazine yields hydrazones of the aldehydes[88].

Lithium tetrahydroaluminate, sodium tetrahydroborate, Grignard reagents, and methyl-lithium have been used to reduce the peroxy-products of ozonolysis to alcohols. Greenwood[89] reduced the ozonisation products of oct-1-ene, oct-3-ene, and hept-2-ene in hexane with lithium tetrahydroaluminate, and obtained respectively heptan-1-ol (95%), propan-1-ol + pentan-1-ol (87%), and pentan-1-ol (89%).

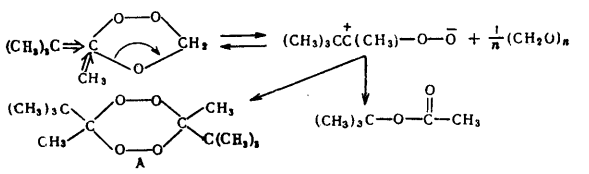
Criegee and Schröder[33] reduced the product of the ozonisation of *trans*-2,2,5,5-tetramethylhex-3-ene at -80° to -100°, which they termed the primary ozonide, with lithium tetrahydroborate, sodium tetrahydroborate, hydrogen iodide in ether, sodium in liquid ammonia, hydrogen on Raney nickel, methylmagnesium bromide, and isopropylmagnesium bromide. Besides the carbinol (neopentanol) found in all cases (other than hydrogen iodide and hydrogen), reduction with sodium in liquid ammonia gave a considerable quantity of a diol (2,2,5,5-tetramethylhexane-3,4-diol). Greenwood[90] obtained α-diols by reducing the ozonides of several other *trans*-alkenes (hex-3-ene, etc.). Sparks and Knobloch[91] reduced the products of the ozonisation of alk-1-enes with a Grignard reagent, and obtained in all cases the corresponding carbinols (products of the addition of the Grignard reagent). In later work Greenwood and Haske[69,92] have shown that, when the ozonide of hex-3-ene is reduced with isopropylmagnesium bromide, the main product is that resulting from addition of the Grignard reagent to propionaldehyde — 2-methylpentan-3-ol — accompanied by propane and propene.

Very little work has been done on the hydrolysis of ozonisation products. In most cases simultaneous formation of aldehydes and acids has been noted. The only mechanism of hydrolysis which has been suggested, in connection with an investigation by Rieche et al.[24] on the ozonide of oleic acid, involves as the first stage cleavage of the ether bridge in the ozonide molecule with formation of a peroxy-diol:

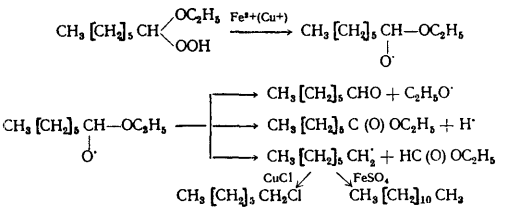


Evidence for this mechanism is the isolation, from the mixture resulting from hydrolysis of the ozonide, of products which the authors identified as 1,1′-peroxydinonanol and 9,9′-dihydroxy-9,9′-peroxydinonanoic acid. In a later paper[15] Rieche put forward the hypothesis that hydrolysis of an ozonide, like its formation, involves an intermediate stage in which a zwitterion is formed.

Very little work has been done also on the thermal decomposition of peroxy-products of ozonisation. Heating the ozonisation products of most alkenes usually gives complicated mixtures of unidentifiable products. Exceptions are the decomposition of naphthalene ozonide, which gives an 87% yield of phthalaldehydic acid when heated in methanol[51], and also the formation of a 69% yield of 2′-formylbiphenyl-2-carboxylic acid when the ozonide of phenanthrene is heated in methanol[50]. Sometimes rearrangements are observed on thermal decomposition. Criegee et al.[31] decomposed the ozonide of 2,3,3-trimethylbut-1-ene and obtained polymers of formaldehyde, a dimeric peroxide (A), and t-butyl acetate. They assumed that the latter two products were formed from a zwitterion containing a t-butyl radical:

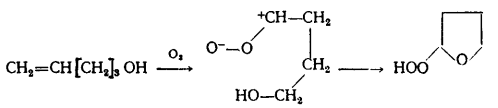


Murai and Sonoda[49] have investigated the reaction of the ozonisation products of alkenes in alcohols. They reduced the product of the ozonisation of oct-1-ene in ethanol (which they termed 1-ethoxy-n-heptyl hydroperoxide) with aqueous solutions of iron(II) sulphate and of copper chlorides, and obtained ethyl formate, heptanol, ethyl heptenoate, hexyl chloride (in the case of cuprous chloride), and dodecane (with ferrous sulphate). Homolytic breakdown of the hydroperoxide was suggested as the reaction mechanism:

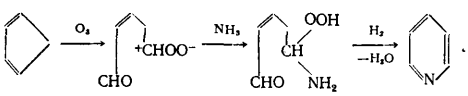


Diaper and Mitchell[93] ozonised ethyl undec-10-enoate in ethanol, subjected the product to alcoholysis at 28–170°, and obtained diethyl sebacate as the main product. They showed that the ester was formed mainly as a result of rearrangement of an alkoxy-hydroperoxide.

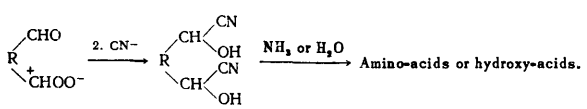
Several interesting reactions occur in the ozonisation of alkenes containing other functional groups, and also when ozonisation takes place in the presence of other compounds. Thus the ozonisation of unsaturated alcohols has been observed to involve cyclisation by the mechanism[94]



A very interesting type of ozonisation has been described by Fremery and Fields[95]. When cyclopentadiene is ozonised in the presence of ammonia or an amine, a hydroperoxide is formed which on reduction and dehydration yields pyridine:



The ozonisation of cycloalkenes in the presence of hydrogen cyanide results in the formation of biscyanohydrins, which can then be converted into amino-acids and hydroxy-acids[96]:



The number of technical processes based on ozonisation is at present limited, and production by these methods is on a small scale. However, the situation in this field should change in the immediate future. This is because of the great amount of research being undertaken and by

the rapid development of the technique of ozonisation. With respect to cost as an oxidant, ozone now occupies the second place after oxygen, which enters the final oxidation product‡.

Work undertaken at the Institute for Organic Chemistry of the German Academy of Sciences in Berlin is of great interest. Bertsch and his coworkers[97] have investigated the ozonisation of alk-1-enes with dodec-1-ene as example at temperatures between -20° and +20°. From the results obtained these workers carried out the ozonisation of the Kogasin fractions of the products of the Fischer–Tropsch synthesis (the 200–210°, 210–220°, and 220–235° fractions containing respectively 41%, 36%, and 32% of alkenes, mainly alk-1-enes), followed by decomposition of the ozonides with water vapour and hydrogenation over Raney nickel at 1–2 atma and 20°. Under these conditions aldehydes were reduced to alcohols, while acids remained unchanged. The yields of products obtained from the fractions were 16–19% of acids, 14–18% of alcohols, and 1.5–2.0% of aldehydes.

Thus the alkenes present in the Kogasins have been completely converted into oxygen-containing products. In later work Greiner and Wagner have studied the kinetics of the addition of ozone to alkenes in the liquid phase[98], the way in which formaldehyde is produced in the ozonisation of alkenes containing terminal and non-terminal double bonds[99], the rates of ozonisation of various alkenes[100], the design of ozonisers[101], and methods for the conversion of ozonisation products into acids[102,103].

Among other methods which have found technical application, mention must be made of the synthesis of strychnine[104] and certain hormones[84], and also the syntheses of piperonal from isosafrole and of vanillin from isoeugenol. Indo[83] made a detailed study of the latter two syntheses, established the structure of the intermediate peroxy-compounds, and worked out several reduction methods aimed at obtaining the maximum yields of vanillin and piperonal.

4. METHODS OF ANALYSIS OF PEROXY-PRODUCTS OF OZONISATION

Although the decomposition products of ozonides and peroxides can be determined by widely used and well studied methods, considerable difficulties are involved in analysing the peroxy-products themselves. In isolated cases use can be made of elementary analysis, determination of available oxygen, measurement of molecular weight, etc., the possibility of using a particular method being governed by the properties of the product to be analysed. In the elementary analysis, ozonides of alk-1-enes (from C_4 upwards) burn quite quietly (if the sample does not exceed 5 mg), but do not liberate iodine quantitatively on reaction with potassium iodide; polymeric products of ozonisation deflagrate when an attempt is made at elementary analysis. Molecular weights are best determined cryoscopically in benzene or bromoform, dichloroethane, etc.[105] Rast's method is unreliable, since the substances under investigation often decompose at the temperatures at which determinations are made by this method.

Peroxy-products of ozonolysis can be arranged in the sequence — hydroperoxides > ozonides > dimeric peroxides — according to ease of interaction with iodides. The reaction is quantitative only with hydroperoxides or ozonides which yield ketones on reduction. Ozonides and peroxides which give aldehydes on reduction often undergo rearrangement into carboxylic acids, which results in a diminution in the quantity of iodide oxidised. Dimeric peroxides often react very slowly.

The infrared spectra of ozonides have been investigated in some detail. Briner and his coworkers at first wrongly assigned to ozonides absorption bands in the region of the carbonyl group[106]. It was subsequently shown that these bands were due to contamination with carbonyl compounds formed by decomposition of the peroxy-products[28,41]. Criegee et al.[31] reported that thirteen out of eighteen ozonides contained an absorption band in the range 9.4–9.6 μm in the infrared spectrum, while the remaining ozonides absorbed at 8.8–9.4 or 9.6–10.0 μm. The present Reviewers have detected[41] two absorption bands — at 1110 and 1062 cm^{-1} — with all products of the ozonisation of n-alk-1-enes, and have regarded them as characteristic of the C–O bonds in an ozonide. Riezebos et al.[39] have observed absorption bands at 1110 cm^{-1} with the six isomeric ozonides of methyl oleate, together with bands at 830 and 1320 cm^{-1} with the *cis*- and *trans*-isomers respectively. Privett and Nickell[74] have also reported the same bands in the spectra of the *cis*- and *trans*-ozonides of methyl oleate. Similar differences have been found by Schröder[68] in the spectra of the stereoisomeric 2,2,5,5-tetramethylhex-3--enes. Greenwood and Haske[69,92] have compared the infrared spectra of hex-3-ene ozonide and di-n-propyl peroxide and have found several coincident bands — at 950, 1380, and 1460 cm^{-1} compared with 955, 1375, and 1453 cm^{-1} — for the two compounds. Loan et al.[40] have observed strong absorption at 1080–1110 cm^{-1} in the infrared spectrum of the ozonide of but-2-ene, which they have attributed to the ozonide group.

Calculations based on the tetra-atomic model molecule C–O–O–H have shown[107,108] that the infrared spectrum of a hydroperoxide should contain the bands listed in Table 5. From a study of the infrared spectra of several hydroperoxides and peroxyalkanols in the region of the hydroxyl--stretching vibrations[108] Terent'ev and his coworkers have assigned to vibrations of a free (or an intramolecularly hydrogen-bonded) hydroxyl the values 3580–3560 cm^{-1} for hydroxyl attached to a carbon atom combined with a peroxy-group, and ~3530 cm^{-1} for a hydroperoxy-hydroxyl.

The nuclear magnetic resonance (n.m.r.) spectra have also been studied with many ozonides. The signals obtained in the n.m.r. spectrum at 30 Mc/s with methyl oleate[39] are listed in Table 6.

TABLE 5. Absorption bands (cm^{-1}) in the infrared spectra of hydroperoxides.

Structure	Calc. for COOH	Cumene hydroperoxide	
		calc.	found
C—O—O	586	597	585
CO—OH	834	838	840
O—O	886	888	886
C—O	1156	1285	1270
O—O—H	1321	1324	1325
O—H	3450	3450	3556

‡ The price of ozone per kilogramme is 17 cents in the USA and from 25 pfennigs in Western Germany.

TABLE 6. Signals due to products of the ozonisation of methyl oleate in the n.m.r. spectrum.

Ozonide	1.1 ppm	1.4 ppm	2.3 ppm	3.7 ppm	5.1 ppm
$(CH_3[CH_2]_7CH)_2O_3$	+	+	–	–	+
$CH_3[CH_2]_7CHO_3CH[CH_2]_7COOCH_3$	+	+	+	+	+
$(CH_3OCO[CH_2]_7CH)_2O_3$	–	+	+	+	+

Note. 1.1 – CH_3; 1.4 – CH_2; 2.3 – CH_2COOCH_3; 3.7 – O–CH_3; 5.1 – $CH\langle^{O-O}_{O}\rangle CH$–.

The n.m.r. spectrum of the ozonide of hex-3-ene contained[69] two overlapping triplets with centres at 4.90 and 4.94 ppm, a multiplet at 1.55 ppm, and two very close and overlapping triplets at 0.8 ppm. These signals were attributed respectively to methine, methylene, and methyl protons of the ozonide.

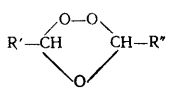
Loan et al.[40] observed in the n.m.r. spectrum of the ozonide of but-2-ene a doublet at 8.65 ppm (CH_3) and two overlapping quartets at 4.72 and 4.78 ppm (*cis*- and *trans*--CH). The n.m.r. spectrum of the ozonide of pent-2-ene showed a multiplet at 5.13 ppm (CH), a multiplet at 8.37 ppm (CH_2), a doublet at 8.65 ppm ($CH–CH_3$), and a triplet at 9.04 ppm ($CH_2–CH_3$). Finally, two overlapping triplets at 4.95 ppm (CH), a multiplet at 8.34 ppm (CH_2), and a triplet at 8.61 ppm (CH_3) were found in the n.m.r. spectrum of the ozonide of hex-3-ene.

Gas–liquid chromatography has also been used for the analysis of ozonides. Schröder[68] has employed a GESF--96 column to separate the *cis*- and *trans*-ozonides of hex--3-ene. Greenwood and Haske[69,92] used a cyanosilicone and diethylene glycol succinate for the same separation.

Thin-layer chromatography is often used for the analysis of ozonides and other peroxy-products of ozonisation, and for their isolation during preparation. A large number of solvents and reagents have been described which can be used for the separation and identification of various peroxides[109,110]. The analysis and identification of the peroxy-products of ozonolysis still remains in general a very difficult task, requiring the combined application of several methods of analysis.

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As long ago as the first decade of this century chemists who had studied the reaction of ozonisation were concerned with the possibility of its wide practical application. The hydrolysis of unsymmetrical ozonides



yields as final products mainly the aldehydes R'CHO and R"CHO and the acids R'COOH and R"COOH. The mixtures of valuable oxygen-containing products obtained by the ozonisation of individual alkenes can be separated comparatively easily.

The ozonisation of alkenes is a rapid process, and the alkenes react completely. However, the explosive properties of many ozonides, and especially of the highly polymeric products obtained on the ozonolysis of alkenes, for many years halted work aimed at the wide practical application of this interesting reaction. Most researches were directed at the use of ozonolysis for studying the structure of organic compounds containing unsaturated bonds.

During this time vast experience has been ascumulated, and a detailed study has been made of the mechanism of the reaction and the chemistry of processes involved in the ozonisation of alkenes and the decomposition of ozonides. The technique of ozonisation has been brought to such a degree of perfection that this reaction can be accomplished to a large extent without danger, so that ozonisation of the higher alkenes can be applied on an industrial scale. An especially important future awaits the processing of higher alk-1-enes into oxygen-containing products – higher aliphatic acids, aldehydes, and alcohols.

The higher C_{7-18} alk-1-enes can be obtained relatively easily by the cracking or the high-speed cracking of alkanes. The resulting products can be separated without special difficulty into individual alk-1-enes from C_7 to C_{16}, which permits the production on their basis, by the application of ozonisation, of several individual oxygen-containing products of immense value to the national economy of the Soviet Union.

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