Translated from *Uspekhi Khimii*, **49**, 2344-2376 (1980) U.D.C. 541.124

Kinetics and Mechanism of the Reaction of Ozone with Double Bonds

S.D.Razumovskii and G.E.Zaikov

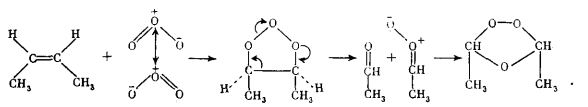
Analysis of the results of recent studies has shown that the reaction of ozone with the double bonds of organic compounds apparently takes place not by a synchronous addition mechanism but through a reversible stage involving the formation of an intermediate complex of ozone with the double bond. The subsequent stages of the reaction involve the formation of a primary ozonide, its decomposition into two fragments, their combination, and a number of other transformations. The properties of the intermediate products, the relationship between the structure of the original alkenes and their reactivity towards ozone, the influence of the nature of the solvent on the direction and rate of the reaction, and the practical application of the reaction of ozone with double bonds in research and chemical technology have been examined. The bibliography contains 205 references.

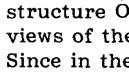
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I. INTRODUCTION

The reaction of the double bond with ozone is one of the most specific reactions of unsaturated organic compounds. It is widely used in preparative synthesis, qualitative and quantitative analysis[1], and chemical technology[2,3]. At the start of the present century, this reaction was used to establish the structure of macromolecular compounds[4], and it is still often used to study the positions of C=C bonds in macromolecules[5,6]. A few years ago, it seemed that the mechanism of the reaction of ozone with a double bond had been fairly well established[2,3,7]. In monographs and reviews, this reaction is dealt with as a classical example of synchronous 1,3-dipolar addition[8-11]:

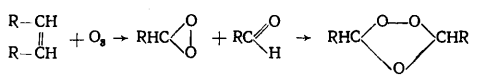


Recent studies have shown, however, that the reaction does not take place synchronously, but involves the reversible formation of an intermediate complex, which has been identified by kinetic and spectroscopic methods. The term 1,3-dipolar addition, introduced by Huisgen[8], is inappropriate when applied to ozone. Huisgen[8] assigned to ozone the structure $\overset{+}{O}-O=\overset{-}{O}$, which does not correspond to present-day views of the electronic structure of the ozone molecule[12-14]. Since in the ozone molecule the dipole moment vector is directed from the central oxygen atom to the terminal atoms , there should be 1,2- and not 1,3-dipolar addition. However, the fact that most alkenes have zero dipole moment, the low value of the dipole moment of ozone (0.53 *D*), the insensitivity of the reaction to polar factors[15], and even, on the contrary, the decrease in the reaction rate with change in the electronegativity of one of the atoms at the double bond[16], indicate that the term "dipolar addition" does not correspond to the character of the reaction being considered.

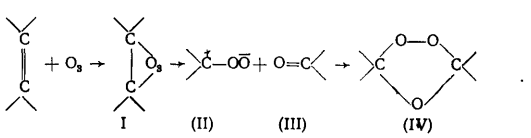
II. MECHANISM OF THE REACTION OF OZONE WITH DOUBLE BONDS

1. Development of Views of the Reaction Mechanism

At an early stage in the studies, Harries[17], Staudinger[18], and Rieche[19] suggested that the reaction involves the formation of a cyclic peroxide

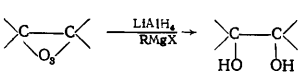


Later, Criegee[20,21] proposed a scheme showing better agreement with known facts about the reaction mechanism:



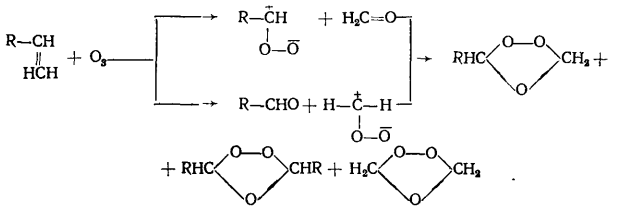
I (II) (III) (IV)

In this scheme, the primary product of the reaction is the so-called molozonide (I), which is unstable at ordinary temperatures and decomposes rapidly to the "zwitterion" (II) and a carbonyl compound (aldehyde or ketone (III)). These intermediate compounds can combine again (after preliminary rotation through 180°) and form a normal ozonide ("iso-ozonide" (IV)). By carrying out the reaction at low temperatures, it is possible to decrease the reaction rate at the molozonide stage, and to observe its transformation into other products[22], for example its reduction to the glycol[23]:

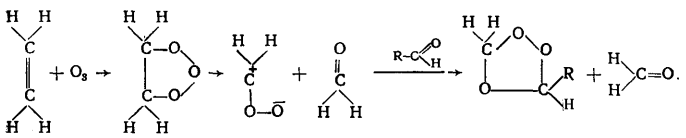


The conjugated formation of the zwitterion–carbonyl compound pair follows from many characteristic features of the reaction. In particular, it is known that the action of ozone

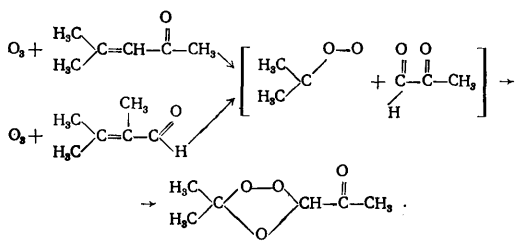
on unsymmetrical alkenes gives the crossed ozonides[24]:



When introduced into a system in which an alkene and ozone are reacting, an aldehyde enters the molecule of the ozonide formed; simultaneously, a carbonyl-containing compound, which is a fragment of the intermediate molozonide, is detected in the system[25]:



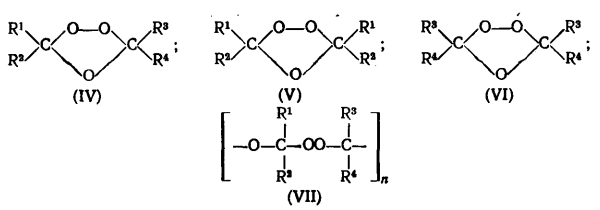
A very elegant confirmation of Criegee's mechanism is provided by the formation of a single final ozonide by the reaction of ozone with two different original alkenes—mesityl oxide and 2,3-dimethylcrotonaldehyde[26]:



Other schemes[24,27] have been proposed in addition to Criegee's scheme, but they have not been adequately confirmed[28,29].

2. Reaction Products

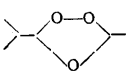
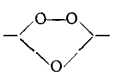
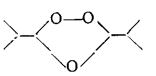
The products of the reaction of ozone with alkenes in solution (in an inert solvent) usually consist of a mixture of the normal ozonide (IV), the crossed ozonides (V) and (VI), and the polymeric ozonides (VII):

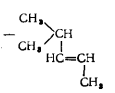


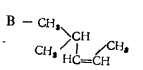
which in accordance with accepted nomenclature can be called 1,2,4-trioxolanes. The reaction mixture contains small quantities of alcohols[30], aldehydes and ketones[31], acids[32], and frequently alkenes oxides[33–36], the concentration of which may be high (up to 90%) in some cases.

Gas chromatography has established the existence of the *cis*- and *trans*-isomers of the normal and crossed ozonides[37,38], which are fairly effectively separated on polyester phases (Table 1) and give different absorption bands in the infrared and PMR spectra[39]. The ratio of the *cis*- and *trans*-isomers in the reaction products is fairly sensitive to the nature of the solvent, the original concentration of the alkene, and the temperature of the experiment.

Table 1. Composition of ozonides, %, from gas–liquid chromatography[24].

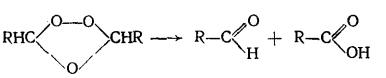
Ozonide	Formula	A	B
Normal			
cis-		32	4.2
trans-		34	4.4
Crossed			
cis-		2.3	5.19
trans-		3.7	6.1
Crossed			
cis-		5.5	12.5
trans-		5.5	6.5

Note: A—original alkene 

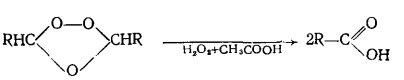
B – 

In early studies of the infrared spectra of ozonides, the maxima in the range 1705–1740 cm^{-1}, due to the absorption by the $\rangle C=O$ group of the decomposition products, were erroneously assigned as characteristic bands of the trioxolane ring[40]. Most ozonides have characteristic absorption bands in the range 980–1100 cm^{-1}.[39,41–43].

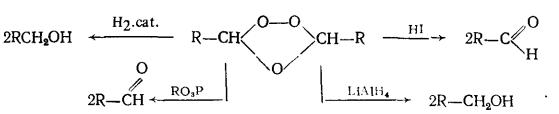
The most typical reactions of ozonides are: thermal decomposition[44,45]



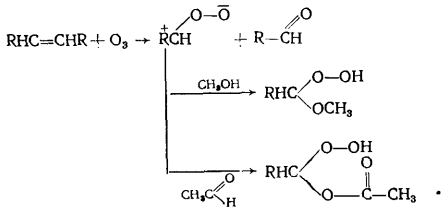
oxidation[46]



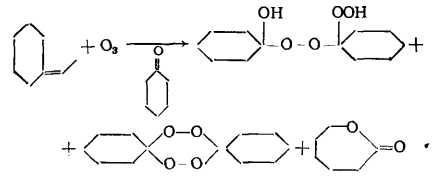
and reduction[46]



When the reaction is carried out in the presence of alcohols, acids, and various other compounds, the products are not ozonides but peroxo-compounds of different character[3,27,46]:



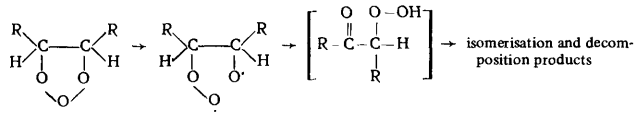
The composition of the peroxo-compounds obtained has not been studied in detail[52,53], but it is known that they are unstable, and capable of further reaction, for example with accompanying carbonyl compounds[54]. When the reaction was carried out in a ketone as solvent, the yield of ozonide decreased from 86.6% to 2.9%, and the chief products were peroxides and lactones[55]



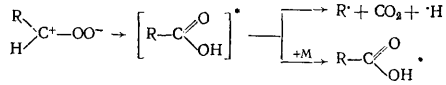
3. Characteristic Features of the Reaction in the Gaseous Phase

The study of the reaction of ozone with alkenes in the gaseous phase has shown that ozonides, which are the chief products of the reaction in solution, are formed in very small quantities in the gaseous phase. The mixture containing CO, CO_2, H_2O, hydrocarbons, acids, and aldehydes, produced by the splitting of the alkene at the C=C bond and further decomposition of the fragments[56–59]. Mass spectrometry has shown that the reaction products contain compounds having mass numbers up to five original molecular units (in particular, for butenes, $M \geq 200$).[60] In the case of halogen-substituted alkenes, the formation of oxides as chief reaction products has been noted[36]. Matrix isolation techniques have shown that the products of the reaction of ozone with ethylene contain not only CO, CO_2, H_2O, CH_2O, HCOOH, CH_3OH, CH_3CHO, and also $\overline{CH_2OCH_2}$, but also the unstable formaldehyde and glyoxal[61]. The reaction is accompanied by chemiluminescence[62], so that it rapidly found practical application in apparatus for determining the concentration of ozone in samples of atmospheric air[63]. The luminescence is due to the presence of the excited species H_2CO (^1A) and OH ($X^2\Pi_i$; $\nu \leq 9$ and $A^2\Sigma^+$).[64,65]

In the proposed reaction schemes, the change in the composition of the products and the formation of excited intermediate species are attributed to radical processes, which begin with the homolytic rupture of the O–O bond of the molozonide[56,66–68]



or as a result of the isomerisation of the zwitterion[44]:



The stoichiometry of the alkene + ozone reaction varies from 1 : 1.4 to 1 : 2, depending on the conditions; when these prevent secondary reactions, the observed stoichiometric ratio is close to 1 : 1.

III. KINETICS OF THE REACTION OF OZONE WITH UNSATURATED COMPOUNDS

1. Gaseous Phase

The reaction of ozone with alkenes takes place readily at all temperatures studied, from −180 °C [43,69] to 300 °C.[70] Its rate is generally limited by the rate of supply of reagents to the reaction site. The elementary reaction of ozone with the double bond of an alkene obeys a bimolecular law[71], whereas the overall process may be described by more complex relationships. In particular, in the gaseous phase there is difference between the kinetics of the reaction in the presence and absence of oxygen[56,58,59,72]. Thus for example, the kinetics of the reaction of ozone with tetrafluoroethylene are described by the relationship[73]:

$$d[O_3]/d\tau = k_1[O_3][C_2F_4] + k_2[O_3]^2[C_2F_4],$$

where

$$\lg k_1 = (8.2 \pm 0.5) - (9500 \pm 700)/2.3\,RT;$$
$$\lg k_2 = (14.6 \pm 0.4) - (10100 \pm 600)/2.3\,RT$$

(k_1 and k_2 in litre mole^{-1} s^{-1} units), and the reaction of ozone with allene is described by the relationship[74]:

$$d[O_3]/d\tau = k'_1[O_3][C_3H_4] + k'_2[C_3H_4][O_3]^2/[O_3]_0,$$

where

$$\lg k'_1 = (6.0 \pm 0.7) - (5500 \pm 1000)/2.3\,RT;$$
$$\lg k'_2 = (6.9 \pm 0.7) - (6200 \pm 800)/2.3\,RT.$$

In both cases the second term takes account of the reaction of the intermediate products with ozone, responsible for its chain decomposition.

Table 2. Rate constants (10^{-3} k, litre mole^{-1} s^{-1}) for the reaction of ozone with alkenes in the gaseous phase at 25 °C.[56,57,71,74–80]

Alkene	Data from Ref.75	Data from Ref.76	Data from Refs.56,57,77–79	Alkene	Data from Refs.57,71, 77, 80
Ethylene	1.6±0.2	1.8	1.6[77]; 0.8[78]; 1.02[57]	Propene	7.1[57]
But-1-ene	6.2	3.9	—	Allene	0.09[74]
trans-But-2-ene	260±40	3	29[78]	Butadiene	4.5[57]
cis-But-2-ene	200	17	63[56]	1,1-Dichloroethylene	0.0022[71]
Isobutene	14±2	3.6	3.7[78]; 0.49[79]; 5.4[56]	1,2-Dichloroethylene	0.24[79]
2-Methylbut-2-ene	450	—	—	Tetrafluoroethylene	31[80]
Trimethylethylene	—	12	—	Hexafluoropropene	1.3[80]
Cyclopentene	—	4.6	61[77,78]	Octafluorobutene	1.6[80]
Pent-1-ene	—	3.9	3.2[77]; 4.5[78]		

Table 2 gives the rate constants for the reaction of ozone with alkenes having different structures. The data in Table 2 do not make it possible to establish a relationship between

the structure of an alkene and the rate of its reaction with ozone; moreover, the data given by different authors sometimes differ considerably (for example for *cis*- and *trans*-but-2-ene). The temperature dependence of the reaction rate has been used to find the activation energies of the process and the pre-exponential factors for a number of alkenes (Table 3). The high rate constants and low activation energies readily explain why the unsaturated components of a contaminated atmosphere are decomposed to the extent of more than 50% by atmospheric ozone, despite the fact that both the ozone and the unsaturated hydrocarbons are present in the atmosphere in small quantities[61,83]. This reaction, together with the reaction of ozone with SO_2 and NO_x, facilitates the formation of photochemical smog in large cities, and usually appears as one of the key reactions in the overall model describing the dynamics of the urban atmosphere[84,85].

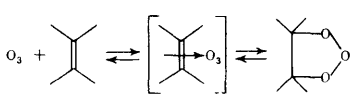
Table 3. Parameters of the Arrhenius equation for the reaction of ozone with alkenes in the gaseous phase*.

Alkene	$10^{-5}A_0$, litre mole^{-1} s^{-1}	E, kcal mole^{-1}
Ethylene	0.0016[77]; 16[75]; 54[81]; 3.2[79]	4.2±0.4[77]; 4.0±0.4[75]; 2.6[81]; 4.9[79]
Propene	0.00037[81]; 2.9[79]	1.9[81]; 3.9[79]
Butene	18	1.7
trans-But-2-ene	3.6[75]; 2.6[79]; 35	0.2±0.3[75]; 2.3[79]; 1.1
cis-But-2-ene	19	0.96
Isobutene	14[75]; 19	2.8[75]; 1.7
2,3-Dimethylbut-2-ene	17	0.82
Hex-1-ene	0.061[77]	

*The values without references are taken from Ref. 82.

2. Kinetics of the Reaction in Solution

In the examination of the reaction in the gaseous phase, it was noted that the reaction of ozone with a double bond is often complicated by side reactions. For the reaction in solution, in the case of simple alkenes, a stoichiometric reagent ratio of 1 : 1 is typical, and more than 95% of the products are formed by a single reaction path. This means that the rate of consumption of the starting materials characterises the reactivity of the ozone–alkene system. Experiments at low temperature, where the intermediate products can accumulate in large quantities and, after evaporation of the system, can regenerate the starting materials to be observed:



have shown that the contribution of the back reactions may be neglected. In a first approximation, the kinetics of the reaction in solution are described by a bimolecular law (Fig. 1).

The published reaction rate constants have been obtained by three methods: by measuring the relative rate of consumption of the alkene being studied, relative to a standard compound[86]; by measuring the rate of absorption of ozone from a gas stream[32]; and by the stopped-flow method[87]. The reaction rate constants in solution are more than an order of magnitude greater than those for the gaseous phase. This may be due to the experimental difficulty of measuring the rates of the rapid gas-phase reactions. Theory does not yet give an unambiguous answer to the question of the ratio of the rate constants in bimolecular reactions in the liquid and gaseous phases[88,89], although it can explain the decrease in the rate constant. For slow processes, such as, for example, the reactions of ozone with saturated hydrocarbons, the rate constants are similar for the solution and the gaseous phase[90].

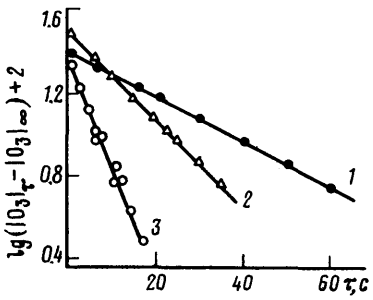
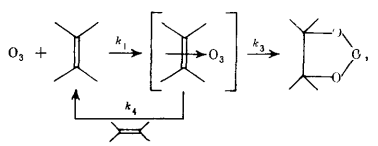


Figure 1. Kinetics of the reaction of ozone with vinylidene chloride in CCl_4 at 20 °C and different initial concentrations of vinylidene, M: *1*) 1×10^{-3}; *2*) 2×10^{-3}; *3*) 5×10^{-3}.

A study of the dependence of the reaction rate on the concentration of the alkenes over a wide concentration range showed that the kinetics of the reaction are described only approximately by the bimolecular law. The experimental data show best agreement with the scheme[3,91]:



in which a new reaction has been introduced—the reaction of the intermediate ozone–alkene complex with another alkene molecule, leading to decomposition of the complex to the starting materials. The observed rate constant k_{obs} is related to the rate constants of the first and subsequent stages by the equations ([Alkene] is the concentration of the alkene):

$$k_{obs} = k_1 k_3/(k_3 + k_4[\text{Alkene}])$$

or

$$1/k_{obs} = 1/k_1 + k_4[\text{Alkene}]/k_1 k_3.$$

Fig. 2 gives as an example the time dependence of the concentration of ozone in the gas stream at the outlet from a reaction vessel containing a solution of acrylic acid (AC), and the dependence of $1/k_{obs}$ on [AC], calculated from these data[32]. The values obtained are $k_1 = 4.2 \times 10^3$ litre mole^{-1} s^{-1} and $k_4/k_3 \doteq 8 \times 10^6$.

This characteristic feature of the reaction must be borne in mind when comparing the results of different studies or when examining the influence of the characteristic features of the structure of alkenes on their reactivity towards ozone.

The temperature dependence of the reaction rate in solution has been studied only for fumaric and maleic acids and maleic anhydride[91]; in the range 17–42 °C, the activation energies are 3, 6, and 6 kcal mole^{-1}, and the pre-exponential factors 1.6×10^6, 77.2×10^6, and 9.7×10^6 litre mole^{-1} s^{-1}

respectively. The rates of the reactions of non-substituted alkenes with ozone are greater by 2–3 orders of magnitude than that for fumaric acid, and the activation energies are 0.5–2 kcal mole^{-1}, which explains the weak influence of temperature on the reaction rate.

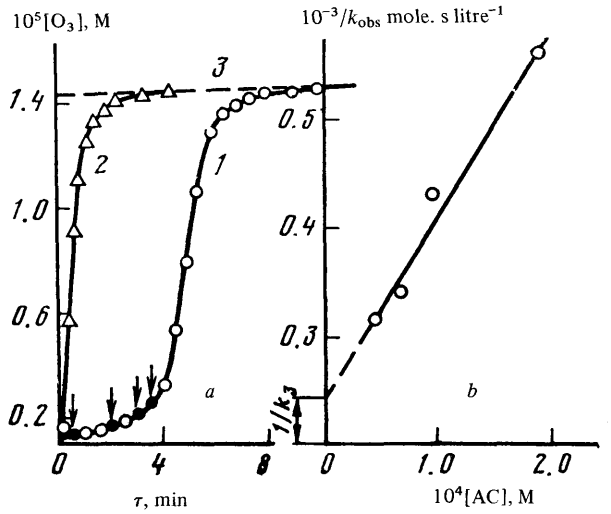


Figure 2. Time dependence of the concentration of ozone at the outlet from the reaction vessel (*a*) and plot of $1/k_{obs}$ against the concentration of acrylic acid (*b*): *1*) 2×10^{-4} M acrylic acid; 2) CH_3COOH; 3) concentration of ozone at the inlet to the reaction vessel, CH_3COOH, 20 °C. The arrows indicate the points used to calculate k_{obs}.

The experimental activation energies typical of the reactions of ozone with unsaturated compounds lie in a range which is not favourable for interpretation; their orders of magnitude do not differ greatly from those of many contributions which are usually difficult to incorporate and which are neglected at values of $E_{expt} \geq 10$ kcal mole^{-1} [92] (these contributions include the energy of reorientation of the solvation layers, the thermal energy of the molecules, etc.). Finally, in the range of these values it is in general difficult to expect that E_{expt} will be independent of temperature, since by definition, $E_{expt} = E_0 + 1/2RT$, where E_0 is the height of the potential barrier at 0 K.

Table 4 shows that low-molecular-weight alkenes having a terminal double bond (hex-1-ene, oct-1-ene, and octadec-1-ene) react with ozone at similar rates. On going to compounds having a C=C bond in the interior of the molecule (hex-2-ene, methyl oleate), there is a considerable increase in the reaction rate. Increase in the number of alkyl substituents on the carbon atoms at the double bond leads to an increase in the reaction rate (compare, for example, hex-1-ene and 2-methylpent-2-ene, acrylic and methacrylic acids, polybutadiene and polyisoprene). C_5–C_{12} cycloalkenes having one C=C bond react at similar rates, irrespective of the size of the ring, and, apparently, slightly less rapidly than a compound having a $\diagdown\!\!\diagup C{=}C \diagdown\!\!\diagup$ bond in an open chain (for cyclohexene, $k_1 = 4 \times 10^5$, compared with 1×10^6 for methyl oleate). The introduction of a phenyl substituent leads to an increase in the reaction rate, and not to a decrease, which might have been expected from the direction of the inductive effect of the phenyl ring. Increase in the number of phenyl groups (styrene–stilbene–1,1,4-tetraphenylbutadiene) has almost no influence on the reaction side.

Table 4. Rate constants for the reaction of ozone (litre mole^{-1} s^{-1}) with different unsaturated compounds in CCl_4 at 20 °C.[93]

Compound	$10^{-5}k_1$	Compound	$10^{-5}k_1$	Compound	k_1
Ethylene	0.4	Norbornene	5	Maleic acid	7.8
But-1-ene	1.3	Styrene	3	Fumaric acid	1.5
cis-But-2-ene	1.63	Stilbene	1.8	Maleic anhydride	14.1
Isobutene	0.97	1,4-Diphenylbutadiene	0.9	2,6-Dimethylhept-2-ene-carboxylic acid	2800
1,3-Butadiene	7.4	1,1,4,4-Tetraphenyl-butadiene	0.8	Vinyl chloride	1180
Pent-1-ene	1.4			Allyl chloride	8500
2-Methylbut-2-ene	5	Acenaphthene	2.2	Bis-1,2-dichloro-ethylene	35.7
Hex-1-ene	1.4	Acrylic acid	0.042		
Hex-2-ene	5	Methacrylic acid	0.078	Vinylidene chloride	22.1
2-Methylpent-2-ene	5	Methyl methacrylate	0.078	Trichloroethylene	3.6
Oct-1-ene	1.3	Oleic acid	10	Tetrachloroethylene	1.0
Octadec-1-ene	1.8	Methyl oleate	10	2-Bromopropene	2800
Cyclopentene	4	Polybutadiene	0.6	Acrylonitrile	100
Cyclohexene	4	Squalene	7.5	Tetracyanoethylene	0.4
Cyclododecene	4	Natural rubber	4.4	1,1,2-Triphenyl-2-nitroethylene	3.6
Cyclododeca-*trans*-1,5,9-triene	3.5	Gutta percha (*trans*-polyisoprene)	2.7		
		Polychloroprene	0.042	1,1-Diphenyl-2,2-dinitroethylene	0.7

The reaction of ozone with an unsaturated compound can be regarded as the reaction of an electrophile with a donor. Thus the introduction into the molecule of electronegative substituents such as Br, $Cl-Cl\!\!\overset{O}{\diagup\!\!\diagdown}\!\!OH$, and NO_2 decreases the electron density in the π-bond and leads to a significant decrease in the rate of the reaction with the corresponding compound. Comparison of macromolecular compounds with their low-molecular-weight analogues readily shows that the reaction rate constants of the polymeric products are lower (compare polybutadiene with methyl oleate and cyclododeca-*trans*-1,5,9-triene or polyisoprene with squalene and 2-methyl-2-ene).[94] A distinct difference is also observed between *cis*- and *trans*-isomers (maleic and fumaric acids, cyclohexene and cyclododeca-*trans*-1,5,9-triene, gutta percha and natural rubber).

The ozone molecule is small, so that steric factors do not play a significant role in the reaction. In only one of the cases in Table 4 is it possible to establish anomalies in the rate which might be attributed to steric effects. Comparison of the reaction rate constants of acrylic, methacrylic, and 2,6-dimethylhept-2-enecarboxylic acids (4.2×10^3, 7.8×10^3, and 2.8×10^3 litre mole^{-1} s^{-1} respectively) with allowance for the inductive effect of the substituents (the method for taking account of this effect is described below) shows that in the absence of steric hindrance, the reaction rate constant for 2,6-dimethylhept-2-enecarboxylic acid should be 7.8×10^3–1×10^4 litre mole^{-1} s^{-1}, whereas the experimental value is smaller by a factor of three.

3. Correlation Between the Structure of an Unsaturated Compound and the Rate of Its Reaction with Ozone

Table 4 shows that the rates of the reactions of ozone with alkenes have structures which differ considerably. For example, for oleic acid and tetracyanoethylene the values differ by more than six orders of magnitude. It is therefore very important to establish the quantitative relationship between the structure of an alkene and its reactivity to ozone, so that this relationship can be used for approximate estimates in work with new substances.

The first attempt in this direction was made by Cvetanovic and Williamson[86], who found a linear relationship between the logarithm of the rate constant and the ionisation potential of chlorinated ethylenes (Fig.3). In spite of the existence of a comparatively simple relationship, this approach cannot be regarded as successful, chiefly because a change in the potential by a small amount (<0.1 V) is accompanied by a change of several orders of magnitude in the reaction rate, and this makes the practical application of the observed relationship difficult. Moreover, the ionisation potential is a generalised characteristic of the molecule as a whole, and in the case of complex molecules, this relationship is not fulfilled in simple form. Distant parts of the molecule, which do not influence the reactivity of the C=C bond, make their contribution to the overall value of the potential.

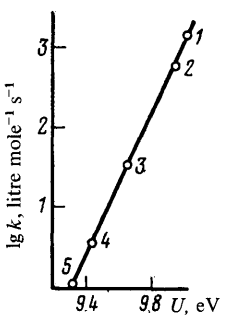


Figure 3. Plot of lg k against the ionisation potential for chlorinated ethylenes: *1*) C_2H_3Cl; *2*) *trans*-1,2-$C_2H_2Cl_2$; *3*) *cis*-1,2-$C_2H_2Cl_2$; *4*) C_2HCl_3; *5*) C_2Cl_4.

The rule that there is a linear relationship between the free energy changes, which establishes a semi-quantitative relationship between the rate constants and the inductive effects of a substituent at the reactive centre of molecules[95,96], is fulfilled for the decomposition of molozonides[97] and ozonides[98], and slightly less satisfactorily for the reaction of ozone with substituted alkenes[93]:

$$\lg(k_i/k_0) = \rho\sigma_{lit},$$

where k_0 and k_i are the rate constants for the reactions of ozone with the C=C bond of a compound taken as standard and the compound containing the substituent being studied, X_i; σ_{lit} is the inductive constant of the substituent, taken from published data, and ρ a proportionality coefficient, called the "sensitivity of the series". The standard compound chosen was ethylene, for which there are no substituents apart from hydrogen at the C=C bond. The plot of $\lg(k_i/k_0)$ against σ_{lit}, constructed from the data in Table 4, is given in Fig.4. In the set of compounds given, a significant deviation from the overall linear relationship is shown by the compounds containing phenyl substituents (styrene, stilbene), and maleic and fumaric acids. Since the rates of the reactions of ozone with acids and their methyl esters are identical (oleic acid and methyl oleate, methacrylic acid and methyl methacrylate), the values of σ_{lit} for the methyl esters were taken as equal to σ_{lit} for the acids (0.265).

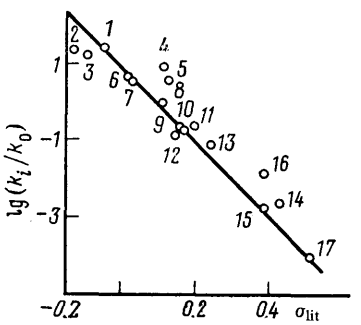


Figure 4. Plot of $\lg(k_i/k_0)$ against the inductive constant of the substituent[93]: *1*) methyl oleate, *2*) methylpent-2-ene, *3*) hex-2-ene, *4*) styrene, *5*) stilbene, *6*) hex-1-ene, *7*) octadec-1-ene, *8*) ethylene, *9*) methyl methacrylate, *10*) methacrylic acid, *11*) allyl chloride, *12*) 2-bromopropene, *13*) acrylic acid, *14*) acrylonitrile, *15*) maleic acid, *16*) fumaric acid, *17*) 1,1,2-triphenyl-2-nitroethylene.

Allowance for the spatial arrangement of the substituents and for electrostatic interactions might apparently improve the agreement between experiment and the model, but even as a first approximation it can be seen that the published values of σ_{lit} can be used to estimate the probable rates of the reactions of ozone with different unsaturated compounds. A negative sign for the coefficient ρ indicates that the reaction of ozone with the C=C bond is electrophilic.

An interesting and as yet insufficiently clear question is the relationship between the reactivities of different groups in a molecule and the degree of deformation of the valence bonds. This deformation may be due to different factors (mechanical forces, steric factors, etc.). The alkenes given in Table 4 include compounds in which the C=C bond is strained for some reason. These include cycloalkenes having large rings (cyclododecene and cyclododecatriene), various norbornenes, and acenaphthene, and unsaturated compounds having bulky substituents at the C=C bond, for example 2,6-dimethylhept-2-enecarboxylic acid in Table 4. Compounds having strained bonds are more reactive than alkenes having an unstrained bond[99]. This is revealed, for example, in the fact that they readily react with diazomethane, whereas alkenes having unstrained C=C bonds do not react in this way. The decrease in the strain in the series of cycloalkenes $C_4 > C_5 > C_6$ coincides with the decrease in the yields of the corresponding pyrazolines[100].

Table 5 gives the published[101] rate constants for the reactions of C_5–C_{12} *cis*-cycloalkenes with ozone. There is a clear relationship between the size of the ring and the rate of the reaction of the compound with ozone. As expected, the reactivity shows a better correlation not with the excess energy of the molecule as a whole but with that fraction of

the strain corresponding to the double bond[101]. Analysis showed[101] that the chief contribution to the change in the reactivity on going from one ring to another is made by the steric factor, determined by the difference between the hybridisation of the carbon atoms at the double bond in the original state and in the activated complex.

Table 5. Rate constants for the reaction of O_3 with *cis*-cycloalkenes (0 °C, CCl_4) and the excess strain of the cycloalkene and the double bond, kcal mole^{-1}.

Ring	$10^{-5}k$, litre mole^{-1} s^{-1}	Cycloalkene	C=C
C_5	4.1	5.9	+2.3
C_6	0.96	0	0
C_7	2.5	5.2	+0.7
C_8	6.0	5.8	−1.6
C_9	3.1	9.4	−0.6
C_{10}	0.73	6.6	−0.7
C_{12}	0.59	—	

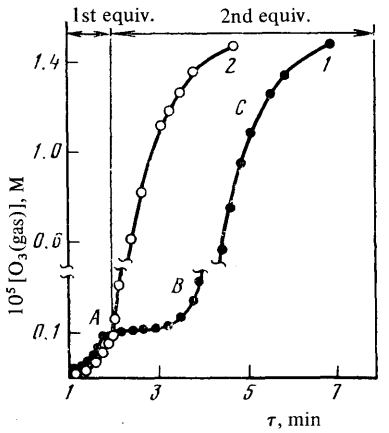
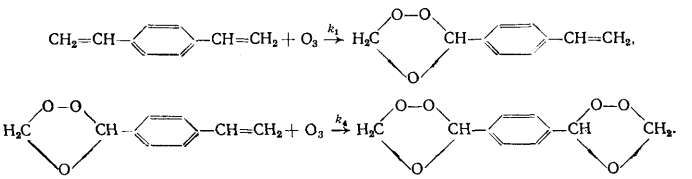


Figure 5. Plot of $[O_3(gas)]$ against reaction time for *p*-divinylbenzene (*1*) and styrene (*2*); *1*) 6×10^{-5} M, *2*) 1×10^{-4} M, CCl_4, 20 °C.

If the alkene molecule contains not one but several C=C bonds, the C=C bonds at a sufficient distance from one another react as independent kinetic units, and the addition of ozone at one of them has little influence on the reactivity of its neighbours. The inductive effect of a substituent usually decreases by a factor of 2.7 through each carbon atom of a saturated hydrocarbon chain[102], so that these influences are of little significance after only 3–4 carbon atoms. In the case of conjugated C=C bonds (1,3-dienes, *p*-divinylbenzenes, etc.), the difference in reactivities due to the structure of the original alkene may be increased by the positive inductive effect of the ozonide formed at a neighbouring group. This can be clearly seen for the case of divinylbenzene (DVB):

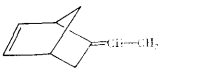
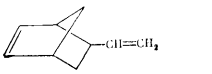
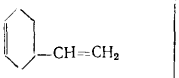
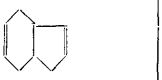
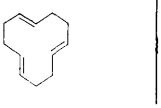


The fact that the reaction takes place in two stages is reflected in the form of the plot of $[O_3(gas)]$ against τ in a bubbler reaction vessel, shown in Fig.5; typical curves for styrene and divinylbenzene are given for comparison. The relationships obtained can be used to calculate rate constants. The rate constant for the reaction of the second double bond of DVB with ozone, k_4, is calculated along section AB using the equation:

$$k_4 = \frac{\omega([O_3]_0 - [O_3(g)]}{\alpha[DVB]''[O_3(g)]}$$

where $[O_3]_0$ and $[O_3(gas)]$ are the concentrations of ozone in the gas flow at the inlet and outlet of the reaction vessel; α the solubility coefficient of ozone; [DVB]" the current concentration of double bonds in the solution; and ω the specific rate of supply of the gas mixture.

Table 6. Rate constants for the reaction of ozone with di- and trialkenes in CCl_4 at 20 °C, litre mole^{-1} s^{-1}.

Compound	Formula	$10^{-5}k_1$	$10^{-5}k_4$
Divinylbenzene		2.1	0.22
Ethylidenenorbornene		3.6	2
Vinylnorbornene		3.3	0.82
Vinylcyclohexene		1.4	0.8
Tetrahydroindene		1.4	1.4
Cyclododeca-1,5,9-triene		3.5	3.5

The values of k_1 are found from the equation

$$k_1 = \frac{\omega([O_3]_0 - [O_3(g)]) - \alpha k_4 [O_3(g)][DVB]_0}{\alpha[DVB]'[O_3(g)]},$$

where $[DVB]_0$ is the initial concentration of divinylbenzene, and [DVB]' the current concentration of DVB molecules having two double bonds. The calculations are possible when k_1 and k_4 differ significantly, and this is the case for divinylbenzene and many other alkenes (Table 6).

For divinylbenzene it is easily possible to follow the change in the reaction rate constant after the addition of one ozone molecule and to show how this change agrees with the general principles of the theory. The rate constant for the reaction of ozone with one C=C bond of the original divinylbenzene, because of the conjugation of the bonds, should be lower than that for styrene, as observed experimentally. When ozone attacks the first bond, the conjugation is broken, so that it might seem that the subsequent stage of the reaction should proceed at a rate close to that observed for styrene (3×10^5 litre $mole^{-1}$ s^{-1}), but the products of the addition of ozone, that is the ozonides, have an appreciable inductive influence on the reaction, so that the second stage is much slower than the first.

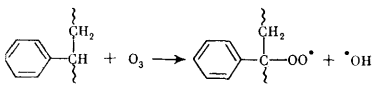
Comparison of the rate constants for the reactions of ozone with ethylidene- and vinylnorbornenes indicates that the initial attack is directed at the double bond in the side chain, since changes in its structure influence k_1, whereas the values of k_4 for the two isomers are identical. The separation of the bonds from one another, and the identical configurations of the immediate environments, make the C=C bonds in cyclododeca-1,5,9-triene equivalent, as shown by the fact that the rate constants for all three stages are identical.

The study of the kinetics of the reactions of ozone with macromolecular compounds is of exceptional interest, since this reaction is the chief cause of the cracking of rubber articles[103]. At the same time, the study of the kinetics of the reactions of ozone with the C=C bonds in macromolecules may give valuable information on the specific influence of the polymeric state on the course of chemical reactions. This question has been attracting considerable attention in recent years[104,105]. Flory[106] put forward the principle that the reactivity of the terminal group or any other group of a polymeric molecule is independent of its length. It is known, however, that certain reactions of polymers take place much more slowly than the reactions of the low-molecular-weight analogues (for example, catalytic hydrogenation), whereas a number of enzyme reactions take place extremely rapidly, but are not shown by the low-molecular-weight compounds[107].

In polymers, approach of the functional groups is possible, and this has a considerable influence on the kinetics of the reactions of these groups[104]. The coiled or straight forms of the macromolecule may create different conditions for the encounter between the reagent and the reacting parts of the macromolecule[108]. The applications of Flory's principle to reactions in which there is no specific interaction between the groups which have approached one another, or hindrance caused by diffusion, have been refined[109]. One of the greatest difficulties in this field is that there are no simple reactions which might serve as models for the study of the specific properties of a macromolecule. In this respect, the reaction of ozone with C=C bonds is exceptionally convenient: it takes place over a wide temperature range, the nature of the solvent has no influence on the reaction rate, and the mechanism of the reaction has been well studied and is the same for low-molecular-weight and macromolecular compounds.

Table 4 gives the rate constants for the reactions of ozone with polymeric compounds and their low-molecular-weight analogues. A good correlation is observed between the reactivities of the monomer and the polymer. In the macromolecular series, the reactivity decreases with change in the inductive effects of the substituents from electronegative to electropositive. It is well known that polychloroprene rubbers are more stable to ozone ageing than butadiene or polyisoprene rubbers. Attempts have been made to relate this increase in stability to a lower reaction rate; the imperfect methods used, however, did not make it possible to detect differences in the rates[110]. The data given in Table 4 show that high stability does in fact correspond to a lower reactivity.

As in the case of the low-molecular-weight alkenes, the *cis*-isomers (natural rubbers) react more rapidly than the *trans*-isomers (gutta percha). The effects associated with change in the length of the macromolecule or the extent to which it is coiled are apparently small, and could not be detected[111,112]. A noteworthy feature is that in all cases the reaction rate constant is smaller by a factor of 1.5–3 than that for the corresponding low-molecular-weight analogue. This characteristic feature cannot be attributed to the specific features of the electrophilic addition of ozone to the C=C bond. The reactions of ozone with the saturated polymers polystyrene and polyisobutene (which take place by a free-radical mechanism[111]):

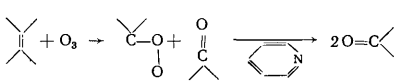


are also slower than those of the low-molecular-weight analogues. The accuracy of the experiment does not make it possible to determine whether the decrease in the rate constant is due to the pre-exponential factor or to the exponential term of the Arrhenius equation (by putting $A_{mon} = A_{pol}$ for $k_{mon}/k_{pol} = 2$, we should have obtained the difference $E_{mon} - E_{pol} = 0.5$ kcal $mole^{-1}$); simple examination shows, however, that the reacting part of the polymer chain should have a lower mobility, since it is joined to extremely long chains. This may decrease the probability of a favourable orientation at the moment of encounter with the reagent.

4. Influence of Solvent on the Mechanism and Kinetics of the Addition of Ozone to the C–C Bond

Many compounds, for example alcohols and acids, can react with the intermediate species, chiefly the zwitterion, altering the direction of the reaction[27,46].

As noted above, in the presence of alcohols and acids, hydroxyalkyl- and hydroxyacylhydroperoxides are formed instead of ozonides[26,113]. When pyridine is used[114], reduction of the zwitterion to the corresponding carbonyl derivative probably takes place:



Saturated hydrocarbons, chloroform, and other halogen derivatives, used as solvents, apparently do not take part in the intermediate stages of the process, although it has been reported that they influence the yield of monomeric and polymeric ozonides[115,116].

An increase in the yield of acids when ozonisation is carried out in esters has been noted[117]. The chemical and physical properties of the system can be altered, sometimes radically, by using a suitable solvent. For example, in the presence of organic acids, gels are not formed in the ozonisation of cyclic alkenes, and the peroxide products of the ozonisation more readily undergo further transformation. In spite of their obvious importance, however, the problems of the influence of the solvent on the mechanisms of the reactions taking place have as yet been little studied, the published data are only preliminary, and the nature of the peroxide compounds and their interconversion, which has been observed by thin-layer chromatography[54], have not been established.

There are particularly few data on the influence of the medium on the rate of the reaction of ozone with alkenes. Only two papers have been published[15,87], giving different results. Razumovskii and Berezova[15] compared the influence of CCl_4, $C_{10}H_{22}$, CH_3COOH, H_2O, and a $CH_3COOH-H_2O$ binary mixture on the rate of the reaction of ozone with acrylic acid; the dielectric constant ranged from 2 to 80; in all cases the reaction rate constant was independent of the nature of the solvent. Henry and coworkers[87] studied the rate of the reaction of ozone with substituted stilbenes in solvents of different polarity (from CCl_4 to CH_3CN); in all cases, the reaction rate increases by a factor of 2–3 on going from CCl_4 ($\varepsilon = 2.24$) to CH_3CN ($\varepsilon = 37.4$). Since Razumovskii and Berezova[15] studied a wider range of ε and used a relatively unreactive alkene (which reduced the experimental difficulties), and since for the closest analogue of the reaction—the reaction of ozone with a C≡C bond—it has also been found that the polarity of the medium has no influence on the reaction rate[118], it may be assumed that the reaction rate depends little or not at all on the solvent.

The fact that the polarity of the solvent has no influence on the reaction rate is in good agreement with the suggestion that the reaction involves a weak intermediate complex in which there is no appreciable transfer of electron density from one partner to the other, so that there is no significant rearrangement of the solvation layer.

IV. INTERMEDIATE STAGES IN THE ADDITION OF OZONE TO ALKENES

The intermediate stages of the reaction of ozone with unsaturated compounds, and the properties and structure of the labile intermediate products, are being studied intensively[28,29,32,119–127]. It still cannot be said that all the characteristic stages of the process are known, but the key reactions have been determined.

This section will examine the qualitative and quantitative characteristics of the stages of the scheme[1] given below. In the reaction of ozone with alkenes in solution, the first stage of the reaction is apparently the formation of a complex of ozone with the C=C bond of the alkene[28,91]. Its formation has been detected from the colour of the solution[7,28], the kinetic characteristics of the reaction[3,91], and the PMR and infrared spectra[43]. In the complex, both partners retain character and can be separated by decomposing the complex. At a low temperature, the reaction can be held at the stage of complex formation, appreciable quantitaties of which can be accumulated[7,119]. This means that the principal activation barrier to the reaction lies on the reaction coordinate after complex formation, as represented schematically in Fig.6. The complex has characteristic adsorption bands in the range 700–1000 cm^{-1}, which disappear rapidly with increase in temperature[119,120].

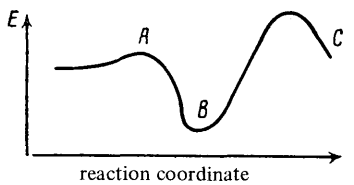
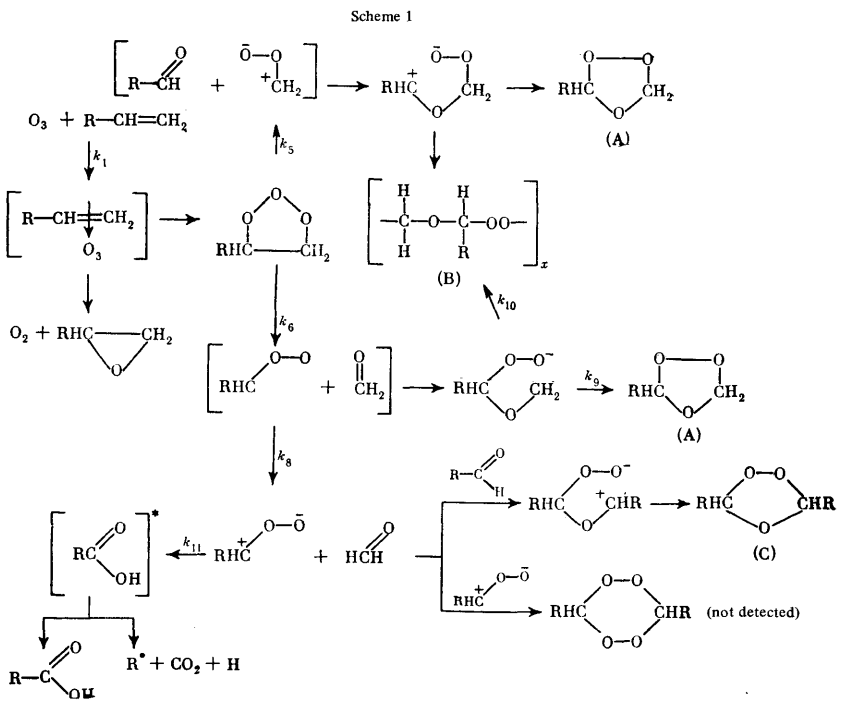
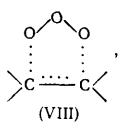


Figure 6. Change in the potential energy of the system in the transformation of the original reagents into the primary ozonide; *B* corresponds to the formation of the complex.

Scheme 1

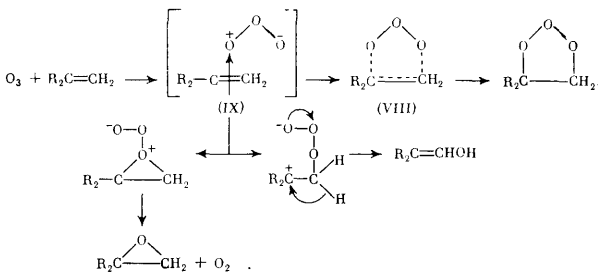


Only tentative conclusions can be reached about the structure of the complex formed. There are serious objections to structure (VIII)



(VIII)

which would correspond to the idea of synchronous 1,3-dipolar addition. It does not explain the mechanism of formation of ozides and vinyl alcohols by the action of ozone on branched alkenes[128]. A scheme including the intermediate formation of a π-complex with a terminal oxygen atom in ozone (IX) has been proposed:

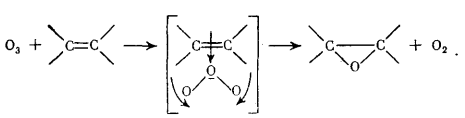


The qualitative character of the data makes it impossible to determine whether (VIII) is formed from (IX) or whether they accumulate in parallel, as suggested by Hull and coworkers[129]. Moreover, the polar structure assigned to (IX) contradicts the above conclusion that the medium does not influence the reaction rate[15]. The kinetic data indicate that in the transition state *A* (Fig.6) and the first intermediate complex, which has a similar structure (corresponding to the minimum *B* in Fig.6), the displacement of charges is slight, so that the solvation does not differ significantly for the original state and the transition state. Quantum-mechanical calculations also show that the formation of open complexes of type (IX) is unfavourable[127]. If it is assumed that the occupied molecular orbitals of ozone in the ground state $^1A_1$ have the configuration

$$O_3[(\text{core})(4b_2)^2(6a_1)^2(1a_2)^2],$$

and that the lowest unoccupied molecular orbital is $2b_1$,[12] it is found that in electrophilic reactions the largest coefficient of the AO corresponds to the central oxygen atom. In other words, electrostatic and polarisation factors favour the formation of a complex in which the optimum overlap of the π-orbital of the alkene and the lowest unoccupied molecular orbital of ozone corresponds to the crossed structure of the complex (Fig.7).

The formation of both the molozonide (for transverse displacements of the original components) and other products from the crossed complex can readily be represented. In particular, the deformation vibrations of the terminal oxygen atoms can probably lead to the formation of oxides:



The next intermediate product in order of relative stability is the molozonide, which can be accumulated in the system and studied. In most cases, the molozonide retains the stereoisomerism of the original alkene[130,131]. The *trans*-ozonide is much more stable than the *cis*-molozonide: the former can be observed in the system as far as −60 °C, whereas the second decomposes rapidly even at −130 °C;[38,119] the *cis*- and *trans*-isomers also differ in various other properties. Table 7 gives as an example the PMR spectra of the isomeric molozonides obtained from different alkenes.

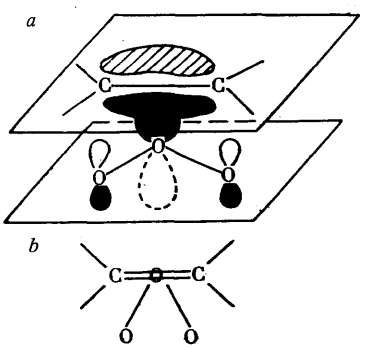


Figure 7. Schematic representation of the ozone–alkene complex: *a*) in the axonometric projection, *b*) view from above.

Table 7. Characteristic absorption bands in the PMR spectra (σ, p.p.m.) of the *cis*- and *trans*-molozonides and normal ozonides from the *cis*- and *trans*-molozonides in CF_2Cl_2 at −130 °C.[131]

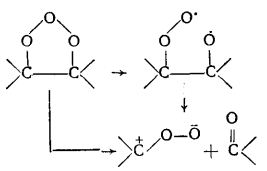
Original alkene	Molozonide	Ozonide
cis-But-2-ene	4.52 (u)*	5.05 (q)*
trans-But-2-ene	4.12 (q)	5.00 (q)
cis-Pent-2-ene	4.35 (m)*	4.93 (m)*
trans-Pent-2-ene	4.08 (m)	4.95 (u)
trans-Hex-3-ene	4.07 (t)	—

Symbols: q = quartet, m = multiplet, u = unresolved, t = triplet; the asterisks mark the data for the *cis*-molozonides.

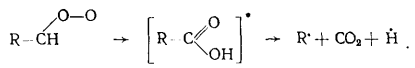
The molozonides have characteristic absorption bands in the range 700–1000 cm^{-1}, which are observed at low temperatures (between −175 °C and −100 °C),[119,121] but which disappear rapidly with increase in temperature to values between −80 °C and −60 °C. The strength of the C–O bond in the molozonide has been estimated as 45 kcal $mole^{-1}$.[132] The molozonides can be reduced to the corresponding diols by the action of an alkylmagnesium bromide or other reducing agents on the products of the reaction of ozone with the alkene at low temperature[123,133]. The first proof that the reaction involves the formation of molozonides involved this reaction.

The molozonide is unstable, and readily decomposes to give two fragments—the zwitterion and a carbonyl compound. It may be assumed that the reaction involves the intermediate rupture of one of the O–O bonds and the formation of a

biradical

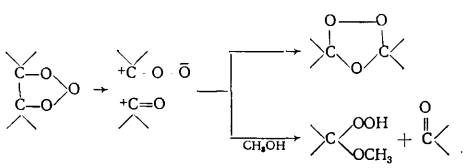


which decomposes rapidly to give the zwitterion and the carbonyl compound. This scheme has been used[66] to explain the high concentrations of free radicals in the reaction of ozone with alkenes in the gaseous phase. Although it has been reported that free radicals have been detected in the reaction of ozone with branched alkenes in solution[134], the accumulated experience in the study of this reaction nevertheless suggests that its principal direction is the direct conversion of the molozonide into two fragments without detectable radical states. The most probable route for the formation of radicals in solution is the isomerisation of the zwitterion and the subsequent decomposition of the excited molecules[44]:



Since conditions in the gaseous phase are not more favourable than those in solution for the stabilisation of free radicals, yet the rates of the processes of energy dissipation are nevertheless greatly reduced, it is more logical to attribute the increase in the concentration of radicals in the gaseous phase to transformation of the zwitterion and to assume that the mechanism of the decomposition of the molozonide is the same for the liquid and gaseous phases, and involves a non-radical route.

The kinetics of the decomposition of the molozonide have been studied in solution by a chemical method[22] and by PMR spectroscopy[135]. In the chemical method, specimens removed at measured time intervals were mixed with alcohol. The molozonide which had not reacted at this moment was converted to the methoxyhydroperoxide in the presence of alcohol:

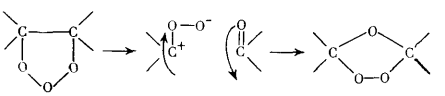


The concentration of the methoxyhydroperoxide in the reaction products gave a measure of the concentration of the molozonide.

The results obtained by the two methods showed good agreement: at -100 °C, the rate constant of the monomolecular decomposition ($k_5 \cong k_6$, see scheme 1) is equal to ~0.1 s^{-1}; the activation energy of the reaction is ~7–8 kcal $mole^{-1}$. The value of the activation energy can be used for a rough estimation of the energy of the O–O bond in the molozonide, which should differ from the activation energy by the difference in the free energies of solvation of the original molozonide and the transition state ($D_{O-O} \cong E$ + 5–10 ≅ 12–17 kcal $mole^{-1}$). The zwitterion formed as a result of the decomposition is an extremely reactive compound, about which very little is known; it can be represented as an aldehyde oxide[38] or as a methylene peroxide[136]. The description of the structure of this intermediate species in the usual symbols presents certain difficulties. It is isoelectronic with ozone, and is apparently a valence-saturated compound, although it is strongly polarised, in view of the difference in the electronegativities of oxygen and carbon.

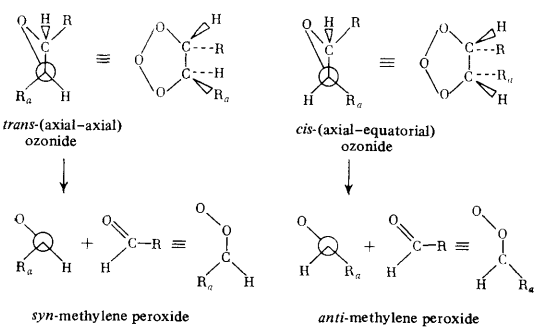
Quantum-mechanical calculations show that the cyclic structure of the zwitterion is energetically more favourable than the open structure[137]. This brings the discussion back to Harries' ideas[17], but at a different qualitative level. A recent study of the reaction of ozone with ethylene in the gaseous phase detected species having a mass number of 46, but the position of their peak did not coincide with that for formic acid[138]. The microwave spectra of this system showed bands at 29.938 GHz and 30.872 GHz, assigned to dioxiran H_2C-OO.[139] For alkenes unsymmetrical with respect to the C=C bond, conditions can be created for the preferential formation of the zwitterion at one of the carbon atoms, depending on the nature of the substituents. In particular, substituents having a positive inductive effect (CH_3, RCH_2, etc.) increase the probability of formation of the zwitterion at the given carbon atom[140], whereas substituents having a negative inductive effect (Cl, , etc.) decrease it. The ratio of the probabilities is described by a relationship of the Hammett type[140]. When both carbon atoms have substituents, the probability of the addition of two oxygen atoms depends on the difference in the inductive constants of the substituents.

The pair (zwitterion and carbonyl compound) formed by the decomposition of the molozonide can combine again extremely rapidly, forming the ozonide (the arrows show the directions of the rotations of the fragments):

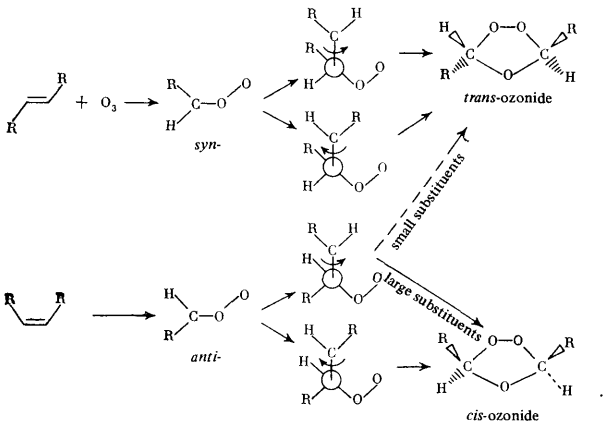


The formation of this compound is preceded by a change in the relative orientation of the fragments (rotation through 180°).

The composition of the final products usually carries valuable information on the processes preceding their formation. Thus analysis of the ratio of the *cis*- and *trans*-isomers in the ozonisation products showed that the zwitterion as it were "remembers" the structure of the original alkene. In spite of the free rotation at the stage of carbonyl formation, the preservation of the structure of the original alkene by the final ozonides is preferred[24,38,141]. This is attributed to the high barrier to rotation in the zwitterion (~29 kcal [136]), which fixes the *syn*- or *anti*-form of the zwitterion:



In the subsequent addition of the carbonyl, a difference betwen the structures of the substituents, together with the *syn*- or *anti*-form of the zwitterion, leads to the formation of *cis*- or *trans*-ozonides[136]:



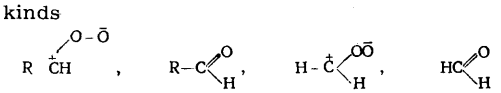
The recently detected influence of complex-forming species on the stereospecificity of the formation of ozonides was explained similarly[126]. A large amount of data has been published on the composition of ozonides[3,7,27,142–149], but only a few papers give a material balance of the principal components[32,41]. Table 8 gives the compositions of the reaction mixtures for several simple alkenes. Judging from the reaction products, most of the zwitterions are able to react with "their own" carbonyl compounds, with which they were formed from the molozonide, that is a clearly defined cage effect is observed[20,144].

Table 8. Composition of the reaction mixture after the ozonisation of the alkenes[32].

Component	Propene	Pent-1-ene	Hex-1-ene	Hex-1-ene
	−78° C			0° C
Normal ozonide (a)	73	67	70	75
Polymeric ozonide (B)	7	8	7	3
Crossed ozonide (C)	20	25	23	22
including:				
macromolecular ozonide	10	15	11	12
ethylene ozonide	10	10	12	10

Note; A, B, and C correspond to the final products of scheme 1, page 1171.

The decomposition of an unsymmetrical alkene gives species of four kinds

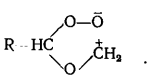


(X) (XI) (XII) (XIII)

in approximately equal proportions (allowance for the inductive effect of the substituent makes it possible to define this more accurately[140]). All the cages of the combination of (X) with (XIII) and of (XI) with (XII), giving A (scheme 1), and of (X) with (XI) and of (XII) with (XIII), giving C, are equally probable. The ratio ([A] + [B] − 0.5[C])/1.5 characterises the fraction of the transformation in the cage, which for all alkenes is close to 0.7. This indicates that the rate of reaction (7) in scheme 1 is comparable with the rate at which the particles leave the "cage". The duration of the existence of the pair of particles in the "cage" can be estimated from Einstein's equation[145,146] $\tau = \frac{1}{6}r^2/D$. For small molecules, $r = 4 \times 10^{-8}$ cm, $D = 10^{-5}$ cm s^{-1}; if it is assumed that the molecules can collide 10–100 times before moving apart, then $\tau = 10^{-11}$–10^{-10} s. For the present case, in the selection of the values of τ, it is also necessary to take account of the fact that an appreciable proportion of the zwitterions reacted outside the cage, forming crossed ozonides. This makes it possible to assume that the value of τ is close to the lower limit of the lifetime of the cage or even lower (10^{-9} s), so that

$$k_7 = 1/\tau = 1 \cdot 10^9 \ s^{-1}.$$

The activation energy of reaction (7) is low, since the cage effect was observed at all temperatures studied (from 30 °C to −78 °C), and the concentrations of the carbonyl compounds and bipolar ions were very low in all cases. Approximately 30% of the total quantity of molozonide decomposition products are able to leave the cage before the start of the reaction; an appreciable proportion leave with an unclosed ring:



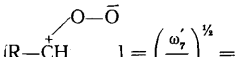
(XIV)

These reactive species move freely in the solution, and are subsequently converted into crossed and polymeric ozonides.

A certain concentration of alkenes and carbonyl compounds is established in the solution. Estimation of this concentration (from the quantity of formaldehyde carried away by the bubbline gas) showed that it is much lower than 10^{-3} M. It can be estimated from the following: $k_8 = 0.3 \times 10^9$; $k_7 = 0.3 \times 10^9$. Since ω_8 is the rate of diffusion, in this case it is possible to use the regular features of diffusion kinetics[147]. The published experimental data[32] then give

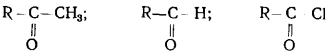
$$k_8 k_7/(k_8 + k_7) = k_7', \text{ from which } k_7' = 0.2 \cdot 10^8 s^{-1},$$

and



$$= \left(\frac{\omega_7'}{k_7'}\right)^{1/2} = \left(\frac{0.3 \cdot 1{,}6 \cdot 10^{-2}}{0.2 \cdot 10^9}\right)^{1/2} = 5 \cdot 10^{-6} \text{ M}.$$

The nature of the substituents at the carbonyl group has a significant influence on the rate of its reaction with the zwitterion. The direction of the influence is the opposite of that observed in the reaction of ozone with the double bond or in the decomposition of the molozonide. Electron-donor substituents decrease the reaction rate, and electron-acceptor substituents increase it. Thus in the series of compounds



the rate of the reaction with the zwitterion increases[3]; the reaction rate constants in the cage, k_7, are 0.3×10^9, 1.0×10^9, and 4.2×10^9 s^{-1} respectively. The zwitterion in solution may react not only with the carbonyl group but also with another zwitterion[7].

In a number of cases, ozonide formation has not been observed at all, and dimeric peroxides and ketones have been obtained[55]. Dimeric peroxides have not yet been detected, however, in the ozonisation products of simple alkenes having an open chain. The formation of polymeric ozonides can be represented as follows: the primary association of the

zwitterion with the carbonyl compound takes place at high rates and without a significant heat change, whereas ring closure is associated with a considerable increase in the order of the system and hence with a decrease in its entropy. The rate of this process is apparently lower than that of the preceding process, and several of these unclosed rings are able to combine with one another before the ring closes. The polymeric ozonides are cyclic formations including an average of about three monomeric units in the case of alkenes having a normal structure[41,148]. The action of ozone on cycloalkenes gives macromolecular three-dimensional products, exhibiting typical properties of polymers[148].

To estimate the probable values of k_9 and k_{10} (see scheme 1), it is possible to make three assumptions: 1) $k_9 \geq k_7$; in this case, k_{10} takes a value $\geq 1 \times 10^{12}$ litre mole^{-1} s^{-1}, which is unlikely; 2) $k_{10} \cong k_7$; in this case,

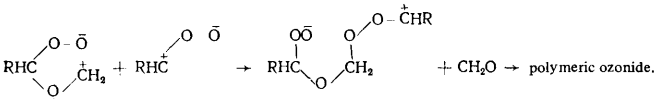
$$[\mathrm{XIV}] \simeq \left(\frac{1.6 \cdot 10^{-2} \cdot 0.1}{10^9}\right)^{1/2} \simeq 1.3 \cdot 10^{-6}\ \mathrm{M},$$

$$k_9 \simeq 1.6 \cdot 10^{-2}/1.3 \cdot 10^{-6} \simeq 10^{-4}\ c^{-1},$$

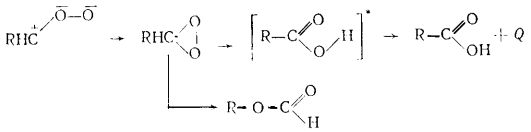
which is quite probable; and 3) both k_9 and k_{10} differ considerably from k_7; in this case it can be established from the experimental data that for −78 °C

$$k_{10}[(\mathrm{XIV})]/k_9 = 0{,}1.$$

The kinetic scheme shows that a decrease in the reaction temperature, an increase in the reaction rate, and the use of polar solvents facilitating an increase in the concentration of (XIV) should increase the formation of the polymeric ozonide. The zwitterion and the carbonyl compound leaving the cage and passing into the solution may also be involved in the formation of polymeric ozonides:



The zwitterion undergoes isomerisation comparatively readily. This reaction provides the principal channel for the formation of acids in the thermal decomposition of ozonides[44]. The isomerisation probably takes place via the cyclic form of the zwitterion:



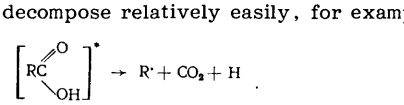
The quantity of free acids formed in the reaction of ozone with the alkene can be used as a measure of the contribution of this reaction to the transformation balance[32].

The unimolecular rate constant for the isomerisation of the zwitterion can be found from the relationship

$$k_{11} = [\mathrm{Acid}]k_7^{1/2}/[\mathrm{Ozonide}]^{1/2}.$$

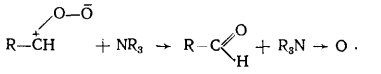
According to published data[32], $k_{11} = (1 \pm 0.8) \times 10^7 \exp\left[\frac{(-6600 \pm 800)}{RT}\right]$ s^{-1}.

The isomerisation of the zwitterions is accompanied by the liberation of 60–80 kcal of energy, which initially is concentrated in the newly formed bonds. The acid molecule is therefore in an excited state (marked by an asterisk in scheme 1) and can decompose relatively easily, for example[44]:



The decomposition takes place more rapidly under conditions in which the dissipation of the energy and the thermalisation of the "hot" molecules are hindered. Thus in the gaseous phase, this process becomes predominant[56–60], whereas in solution at room temperature or lower temperatures, its contribution usually does not exceed 1–3%.[32]

The reaction in the second direction—the splitting of the C–C bond with the formation of esters of formic acid—is slower by about three orders of magnitude, and is observed in the reaction of ozone with branched alkenes[149]. The zwitterion may react with added ammonia, pyridine, or tetracyanoethylene[150]:



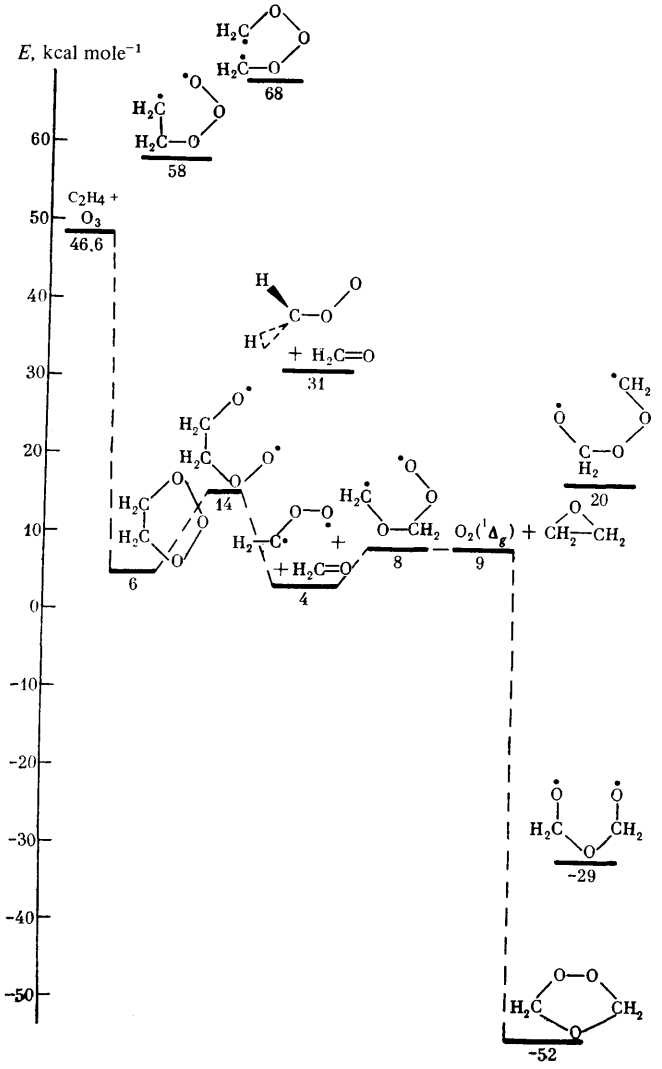
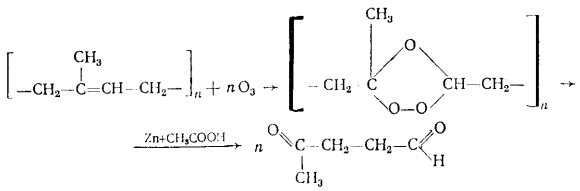


Figure 8. Thermochemistry of ozonisation.

Fig.8 gives the results of thermochemical calculations which make it possible to show the positions of the intermediate species on the reaction coordinate (marked by the broken line relative to the initial and final stages)[136]. In addition to the labile intermediate products mentioned in the text, the diagram shows species whose possible formation has been discussed in the literature. Unfortunately, Fig.8 does not give the complex of ozone with the alkene, for which thermochemical data are not yet available.

V. THE USE OF THE REACTION OF OZONE WITH UNSATURATED COMPOUNDS IN RESEARCH AND TECHNOLOGY

Comparison of the rate of the reaction of ozone with the double bond and with the $-CH_2-$ group of the saturated parts of the alkene molecule shows that they differ by 4–8 orders of magnitude[151]. This makes it possible to use ozone in analysis to determine the number of double bonds and their position in the molecule of an organic compound. Mention must first be made of the classical work of Harries, who determined the structure of various natural polymers, in particular natural rubber[4]:



Subsequently, the rupture of a double bond by ozone has been used repeatedly in the study of the structure of various new polymers and copolymers[5,152–158]. This question has been the subject of several reviews[4,46,104].

The use of ozone to study the processes associated with the formation of unstable products, for example keto–enol tautomerism, has proved extremely effective[1,159].

In the early nineteen-thirties, a process for obtaining high-octane petrol by the dimerisation of propene and butenes was widely developed; the positions of the double bonds in the isomeric dimers were determined from the composition of the ozonisation products[160]. This method proved extremely useful in the study of the structure of lipids, fats, steroids, and other natural compounds[53,161,162].

The combination of ozonisation methods with gas–liquid chromatography increased considerably the possible use of ozone in determining the structure of unsaturated compounds, since it became possible to analyse ultramicro-quantities of the products (~10^{-3}–10^{-6} M). The procedure for these determinations has been described by a number of authors[163,164].

The determination of the position of a C=C bond in the molecule of an organic compound is now well established. It is often necessary to determine the positions of several C=C bonds present together (for example, the 1,2- and 1,4-structures in polybutadienes) and the nature of the terminal groups of the macromolecules of synthetic polymers, to distinguish double and triple bonds, etc. In these cases it is necessary to make a more complete study of the composition of the reaction products or to combine the results of the study of the composition of the reaction products with kinetic data[5].

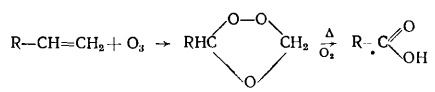
A large proportion of present-day processes in organic synthesis, petroleum chemistry, and polymer chemistry are based on various transformations of compounds containing a double bond. The use of ozone has made it possible to develop control systems which are very rapid and have a very high sensitivity (as far as 10^{-8} M double bonds in the specimen)[165]. They have proved to be particularly effective in the determination of the quality of new saturated copolymers containing small quantities of added dienes, for example the ethylene–propene–diene copolymer (SKEPT), in which the concentration of unsaturated units in the molecule is 0.5–2%, which lies at the limit of the sensitivity of the methods previously used.

In the analysis of the products of the incomplete hydrogenation of fats (margarines), compounds containing halogen atoms or aromatic rings at a double bond, and new polymeric materials such as acrylates or urethanes, the usual iodometric or infrared spectroscopic methods are ineffective, whereas the use of ozone gives good results[151,166,167].

The concentration of ozone in the layers of the atmosphere close to the earth's surface is usually low (10^{-10}–10^{-9} M), but it increases considerably in industrial centres. Ozone plays an important role in the production of photochemical smog, so that the monitoring of atmospheric ozone is included in all ecological programmes[85]. Various methods have been proposed for determining ozone in air[3,168–171]. One of the best methods is that based on the measurement of the intensity of the chemiluminescence produced when ethylene is mixed with a portion of the air being studied[62,63].

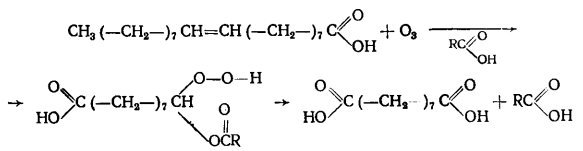
The reaction of ozone with double bonds has also found application in the preparation of many oxygen-containing compounds[26,172–175]. According to published data, a number of technological assemblies are now operating, and new ones are being devloped[26,174,176,177]. The principal direction in this work at present involves the preparation of expensive products from scarce raw material. In these processes, the high selectivity of the reactions of ozone has made it possible to achieve maximum yields.

Ozonisation provides the simplest method of obtaining various acids[178–180]:



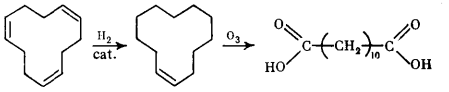
The demand for organic acids is extremely large; they are obtained from plant and animal products or by oxidising saturated petroleum hydrocarbons. The last reaction gives acids containing considerable quantities of undesirable functional groups (keto- and hydroxyacids, lactones, etc.) and having a wide fractional composition. The quality of the acids obtained by ozonisation is much better, and their composition is determined by the original alkene[180,181].

Several methods have been published for preparing adipic[182–184], azelaic[26,185–187], and other dicarboxylic acids[188–191]. The industrial production of azelaic acid is based on the treatment of oleic acid with ozone in nonanoic acid:

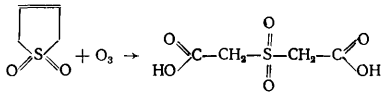


The development of methods for the cyclo-oligomerisation of divinyl[192] and the selective hydrogenation of dimers and

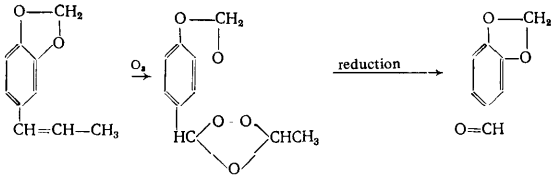
trimers to monocycloalkenes[193,194] makes promising the synthesis of octane dicarboxylic and dodecanedicarboxylic acids[113]:



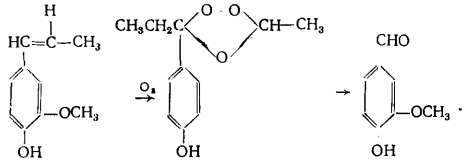
The synthesis of dicarboxylic acids containing heteroatoms in the molecule has been reported[195,196]:



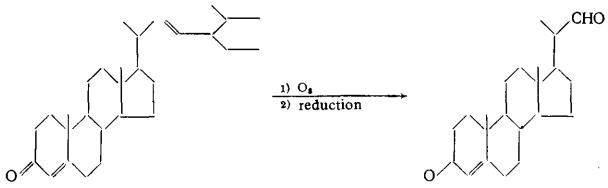
Various aromatic aldehydes have been obtained in good yields, for example heliotropine, used in perfumery and cosmetics[197]:



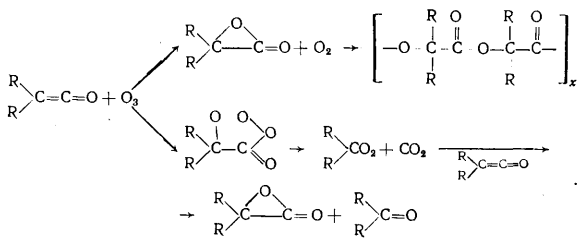
and of vanillin from isoeugenol[198]:



Various steroids in which the double bond in the ring is stabilised by substituents having an appreciable electron affinity give good yields (up to 94%) of aldehydes as a result of bond rupture in the side chain[26,174,199]:



The reaction of ozone with ketenes giving α-lactones, which polymerise spontaneously to give complex polyesters[200,201]. The mechanism of the reactions taking place can be represented by the following scheme:



The synthesis of biologically active compounds, for example glutamic acid from cyclopentadiene[202], various hormones such as cortisone and progesterone from ergosterol (protovitamin D),[203] keto steroids[204], steroids containing heteroatoms[205], and intermediate α,ω-dialdehydes of given stereoisomeric form in the synthesis of tellergons[91], has been described.

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