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The Reactions of Acetals with Ozone

D.L.Rakhmankulov, E.M.Kuramshin, and S.S.Zlotskii

Data concerning the composition of the products of the ozonisation of acetals, the stoichiometry of the process, and the influence of substituents and the structure of acetals on their reactivity, the effect of the polarity of the medium, the activation parameters for the process, and the kinetic isotope effects are surveyed and analysed. At lowered temperatures the process proceeds via a heterolytic mechanism, while with increase of temperature the fraction of ozone consumed due to the formation of free radicals rises.
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I. INTRODUCTION

The reactions of organic compounds with ozone, leading to various polyfunctional oxygen-containing compounds, are of considerable theoretical and practical interest.[1-3] However, the available information about the reactions of saturated hetero-organic compounds with ozone has not so far been surveyed or described systematically. It is known that, in the course of the ozonolysis of saturated oxygen compounds, substances containing carboxy-, carbonyl, and hydroxy-groups are formed.[4-9] The ozonolysis of acetals with linear and cyclic structures proceeds smoothly under mild conditions and with a high selectivity.[10-19] Since acetals can be readily obtained from cheap easily available petrochemical products, their use as the starting materials in organic synthesis is extremely promising. The ozonolysis of 1,1-dialkoxyalkanes and 1,3-dioxacyclanes leads to the formation of esters, alcohols, and glycol monoethers, ozone attacking only the methylene (or methylidyne) group adjoining two heteroatoms.[12,18] The principal publications devoted to this process are summarised and analysed in this review.

II. THE PRODUCTS OF THE OZONOLYSIS OF ACETALS AND RELATED COMPOUNDS

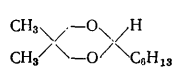
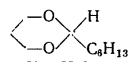
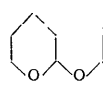
The first communication[11] stating that the reaction of ozones with acetals is rigorously specific, giving rise to quantitative yields of the corresponding esters of alcohols or glycol monoesters, was published in 1971. In later studies by the same workers,[12-16,20-23] a relation was established between the conformation of the acetal group and its reactivity towards ozone. It was shown that the reaction considered is general for acetals having linear and cyclic structures (Table 1).

The nature of the alkyl substituents in acyclic acetals does not influence the composition of the reaction products. However, significant differences are observed between the rates of oxidation; cyclic acetals react much faster than acyclic acetals (Table 1). Thus the complete oxidation of 1,3-dioxolans (I) and (II) required only 10 min, whereas exhaustive ozonolysis of the dimethoxyacetals (VI) and (VII) takes place in 13–15 h. Under these conditions, one mole of ozone reacts with one mole of the acetal, giving rise to one mole of the ester and one mole of oxygen.

The interaction of ozone with linear-cyclic acetals has been studied in relation to tetrahydropyranyl and tetrahydrofuryl ethers.[12,13]

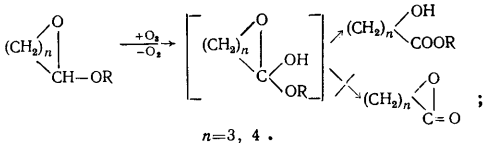
Treatment of 2-alkoxyoxacyclanes with ozone (Table 1) results in the exclusivie formation of esters of ω-hydroxy-acids; lactones and other products were not detected in the reaction mixture.[12,13]

Table 1. Ozonolysis of acetals at −18 °C in ethyl acetate.[11]

No.	Acetal	Product	Reaction time, h	Yield, %
(I)		$C_6H_5COOCH_2CH_2OH$	10*	100
(II)		$C_6H_{13}COOCH_2CH_2OH$	10*	98
(III)		$C_6H_{13}COOCH_2C(CH_3)_2CH_2OH$	1	98
(IV)		$C_6H_{13}COOCH_2CH_2CH_2OH$	2	97
(V)	$C_6H_{13}CH(OC_2H_5)_2$	$C_6H_{13}COOC_2H_5$	8	97
(VI)	cyclo-$C_6H_{11}CH(OCH_3)_2$	cyclo-$C_6H_{11}COOCH_3$	13	98
(VII)	$C_6H_{13}CH(OCH_3)_2$	$C_6H_{13}COOCH_3$	15	91
(VIII)			2	99
(IX)			1	91
(X)			3	91
(XI)			2	95
(XII)			6	85
(XIII)			6	87

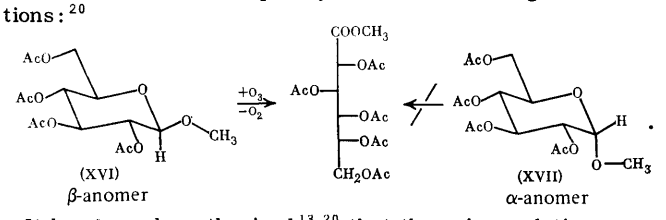
*The reaction time is given in minutes.

The formation of the products of this process is explained by the following scheme:[13]



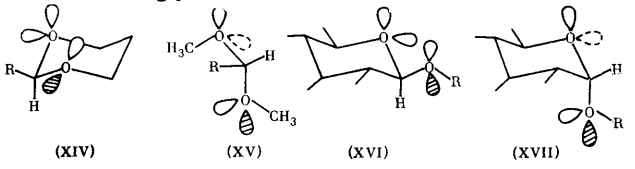
$n=3, 4$.

Subsequently the oxidation of a series of conformationally rigid α- and β-methylglucopyranosides was investigated.[12,20] The β-anomers were oxidised smoothly with ozone, while the α-anomers did not react. For example, methyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (XVI) is converted into methyl 2,3,4,5,6-penta-*O*-acetylgluconate, while the corresponding α-anomer (XVII) is completely inert under analogous conditions:[20]



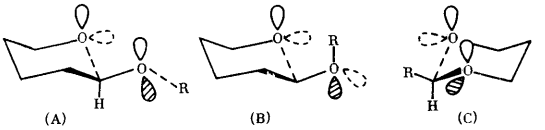
(XVI) β-anomer (XVII) α-anomer

It has been hypothesised[13,20] that there is a relation between the configuration of the acetal group and its reactivity with respect to ozone. For the successful occurrence of the reaction, there should be at each oxygen atom in the acetal an unshared electron pair such that its free orbital is oriented perpendicular to the plane including the C–H bond to be dissociated. This requirement is satisfied by acetals with a dioxan structure (XIV) and the most stable rotational isomers of the β-glycosides (XVI).



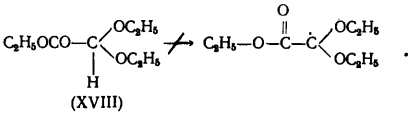
(XIV) (XV) (XVI) (XVII)

In the α-glycosides (XVII), the preferred conformation is that where the orbitals of the oxygen atoms in the ring are not oriented perpendicular to the plane containing the C–H bond and only the second oxygen atom has an orbital with the appropriate orientation; the oxidation with ozone does not therefore occur at an appreciate rate. For the preferred conformation of the linear acetal (XV),[13] the orientation of the oxygen orbitals is analogous to that in the α-glycosides (XVII). In order to interact with ozone, the dialkoxyalkane needs to assume another conformation, which ensures the required orientation of the orbitals (this is impossible for α-glycoside with their rigid chair conformation). However, the equilibrium concentration of any reactive conformer of a dialkoxyalkane is extremely insignificant, because the anomeric effect must be overcome for its formation and the rate of reaction, which depends on the concentration of this conformer, is extremely low. All the possible skewed conformers possible for the acetal group have been examined[20] and for each of them a rigid chemical model was selected and its reactivity with respect to ozone was determined. The experimental results obtained, summarised in a number of studies,[13,20,22,23] established that, of the six *gauche*-conformations possible for the acetal group, only three, namely (A), (B), and (C), are reactive with respect to ozone:



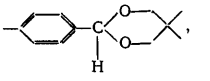
(A) (B) (C)

In these conformers the orbital of the unshared electron pair of each oxygen atom is oriented perpendicular to the plane containing the C–H bond. The results suggested[13] that a positive charge on the carbon atom of the acetal group should be generated in the transition state of the reaction. The appropriate disposition of the orbitals of the free electron pairs of each oxygen atom can readily stabilise such a positive charge. In the presence of the ethoxycarbonyl group this type of stabilisation is impossible and ethyl diethoxyacetate (XVIII) proved to be completely inert with respect to ozone. This rules out the possibility of a free-radical reaction mechanism because the presence of the ethoxycarbonyl group should facilitate the formation of the intermediate dialkoxyethoxycarbonylmethyl radical:



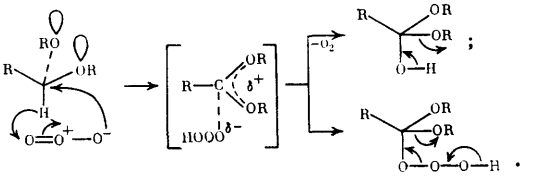
(XVIII)

The study of the reactivities of the acetals of *p*-substituted benzaldehydes



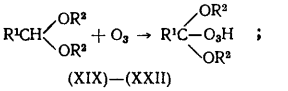
where R = OCH_3, H, or NO_2, showed that electron-donating groups accelerate the reaction, while electron-accepting groups retard it.

The set of the results obtained suggested the following process mechanism[13,20] [see also Section (V)]. Ozone reacts with the C–H acetal bond by a 1,3-insertion mechanism, forming either an α-hydroxyacetal and molecular oxygen or a hydrotrioxide:



These products decompose to an ester of an alcohol. It must be emphasised that ozone is inserted only for the conformation of the acetal group in which the orbital of the free electron pair of each oxygen atom has the antiperiplanar orientation in relation to the C–H bond.

In most investigations it has been suggested that the labile intermediates in the ozonolysis of unsaturated compounds are the corresponding hydrotrioxides.[13,20,24] The first spectroscopic evidence for the existence of hydrotrioxides was obtained in the study of the ozonolysis of ethers.[24] It has been observed recently[17,28] that the interaction of acetals with ozone results in the formation of hydrotrioxides, stable at −50 °C, which have been identified by ^{1}H NMR:



(XIX)—(XXII)

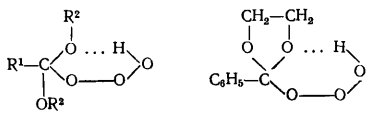
(XIX): $R^1=R^2=CH_3$

(XX): $R^1=CH_3$, $R^2=C_2H_5$

(XXI): $R^1=C_6H_5$, $R^2=CH_3$

(XXII): $R^1=C_6H_5$, $R^2R^2=(CH_2)_2$.

The ^{1}H NMR spectra contain two signals in the region of δ = 13 p.p.m. relative to Me_4Si. Since the position of the signals did not change appreciably on dilution, they were preferentially attributed to the proton of the OOOH group combined into six-membered rings by an intramolecular hydrogen bond:[28]



Although the origin of two signals of the proton in the O_3H group remains obscure, it is of interest to note that a similar observation has been made for the hydrotrioxide of 2-methyltetrahydrofuran.[24] With increase of temperature, both signals tend to merge and broaden. It has been suggested[28] that this splitting may be caused by the presence of two conformations of the hydrotrioxides of acyclic acetals, which is a result of the non-equivalence of the two oxygen atoms in acetals. The acetal hydroperoxides can be used as effective oxidants for organic compounds. It has been shown[25] that the reaction of 1,1-diethoxyethane hydrotrioxide with diphenylamine and 2,2,6,6-tetramethylpiperidine leads to the formation of the corresponding hydroxy-radicals (the diphenylnitroxy-radical and the 2,6,6,6-tetramethylpiperidin-1-yloxy-radical). Under mild conditions, 1,1-diethoxyethane hydrotrioxide rapidly oxidises pyridine to the *N*-oxide and dipropyl sulphide to dipropyl sulphoxide.[26,27]

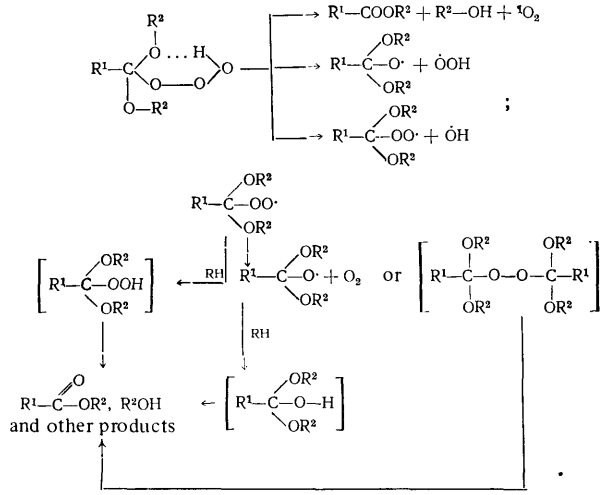
The kinetics of the thermal decomposition of acetal hydroperoxides have been investigated both for the pure substances and for their solutions in diethyl ether and methylene chloride.[17,28] The decomposition follows first-order kinetics. The expressions for the rate constants $k(s^{-1})$ for the thermal decomposition of the hydrotrioxides investigated have the following forms:

$$\begin{aligned}&\text{(XIX)}\quad \lg k = 11.8-67.5/\theta,\\ &\text{(XX)}\quad \lg k = 11.1-60.8/\theta,\\ &\text{(XXI)}\quad \lg k = 15.8-79.6/\theta,\\ &\text{(XXII)}\quad \lg k = 12.2-62.3/\theta,\end{aligned}\qquad \theta = 2.3RT\ .$$

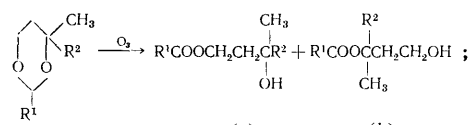
Table 2. The composition of the products of the ozonolysis of 1,3-dioxacyclanes at different temperatures.[29]

Initial compound	Isomer ratio (*a*)/(*b*)		
	−50° C	15° C	50° C
(XXIII)	2:1	2:1	2:1
(XXIV)	2.5:1	2:1	2:1
(XXV)	7:1	3:1	2:1

The low pre-exponential factors for compounds (XIX), (XX), and (XXII) apparently indicate a chain mechanism for the decomposition reaction. All the hydrotrioxides investigated decompose in the temperature range from −40° to +40 °C with formation of singlet oxygen, whose yield (relative to the amount of ozone absorbed) varies from 45 to 80% and depends on the initial compound. In the case of 1,1-diethoxyethane hydrotrioxide (XX), ethyl acetate (0.80–0.85 mole per mole of the ozone absorbed), ethanol (0.70–0.75 mole), water, acetaldehyde, acetic acid, ethyl formate, diethyl carbonate, as well as small amounts of gaseous substances, probably ethane and methane, were detected among the reaction products. The presence of two types of peroxy-compounds, which were not finally identified but are tentatively believed to be an alkyl hydroperoxide and a dialkyl peroxide, was also observed. Apparently the formation of a considerable proportion of ethyl acetate and ethanol together with singlet oxygen is due to the non-radical decomposition of the hydrotrioxide, while the presence of the other two products in the reaction mixture can be accounted for by a free-radical decomposition mechanism:[17]



The reactions of asymmetric 1,3-dioxacyclanes with ozone have been studied in relation to 4-methyl-1,3-dioxan (XXIII), 2,4-dimethyl-1,3-dioxan (XXIV), and 4,4-dimethyl-1,3-dioxan (XXV) in the temperature range from −50° to +50 °C.[29] The reaction products (Table 2) consist of a mixture of the isomeric monoethers (*a*) and (*b*), whose yield relative to the ozone and the substrate which have been consumed reaches 95%:

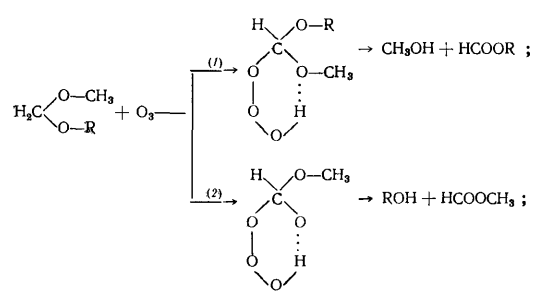


(*a*) (*b*)

R^1, R^2=H (XXIII); R^1=CH_3, R^2—H (XXIV); R^1=H, R^2=CH_3 (XXV).

In all cases the main products are substances with an acylated primary hydroxy-group (*a*). These results can be accounted for by the preferential dissociation of the C(2)–O(3) bond in the intermediate hydrotrioxide,[29] which is caused by the steric repulsion between the hydrotrioxide group and the axial CH_3 group attached to the C(4) atom in the ring.

The interaction of asymmetric linear acetals with ozone has been studied in relation to methoxyalkoxymethanes at −60 °C.[30] Butyl formate, methyl alcohol, butyl alcohol, and methyl formate accumulate simultaneously in the interaction of ozone with butoxymethoxymethane (XXVI). The ozonolysis of methoxypentoxymethane (XXVII) leads analogously to pentyl formate, methyl alcohol, pentyl alcohol, and methyl formate. The results have been explained within the framework of the following mechanism:



R=C_4H_9 (XXVI), C_5H_{11} (XXVII); (*1*):(*2*)=4:1 .

The observed ratio of pathways (*1*) : (*2*) = 4 : 1 can be explained by the preferential formation of an intramolecular hydrogen bond involving the oxygen atom of the OCH_3 group in the intermediate hydrotrioxide, while the steric hindrance due to the C_4H_9 and C_5H_{11} groups diminishes the probability of the formation of a hydrogen bond involving the OR group.

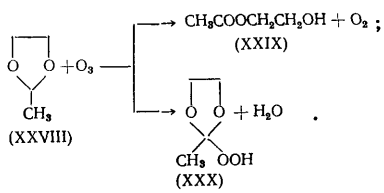
The behaviour of the C–H bond adjoining the three oxygen atoms in relation to ozone has been investigated.[31] Ethyl orthoformate, which is regarded as a derivative of diethoxymethane in which the hydrogen atom has been replaced by the ethoxy-group, was chosen as the object of study. It was established that the main ozonolysis products are diethyl carbonate, ethyl formate, and ethyl alcohol, which accumulate simultaneously:

$$HC(OC_2H_5)_3 + O_3 \begin{cases} \longrightarrow HO_3C(OC_2H_5)_3 \xrightarrow{-O_2} OC(OC_2H_5)_2 + C_2H_5OH \\ \longrightarrow HC(OC_2H_5)_2OCH(O_3H)CH_3 \xrightarrow{-O_2} HCOOC_2H_5 + C_2H_5OH + CH_3CHO \end{cases}.$$

The attack by ozone on the C–H bond adjoining the three oxygen atoms is the main pathway in the process. The reactivity of ethyl orthoformate towards ozone is close to that of diethoxymethane, is twice as high as the reactivity of ethyl alcohol, and is much less than the reactivity of 1,1-diethoxyethane.

III. THE CONTRIBUTION OF RADICAL REACTIONS IN THE OZONOLYSIS OF ACETALS

The results of the ozonolysis of acetals at reduced temperatures (between −78° and 20 °C)[13,29,32,33] clearly demonstrate that the reaction is general and leads to the formation of esters or glycol monoesters with a selectivity not less than 90%. It has been shown[32] that, in the temperature range 20–60 °C, water and organic hydroperoxides, identical to the products obtained in the initiated oxidation of acetals by molecular oxygen, are formed together with the products indicated above. It has also been demonstrated that the reaction of 2-methyl-1,3-dioxolan (XXVIII) with ozone between 20° and 40 °C involves the simultaneous accumulation of the monoester of ethylene glycol (XXIX), the corresponding hydroperoxide (XXX), and water, while at temperatures ≤5° the monoester (XXIX) is virtually the only reaction product (Table 3):



It has also been found[32] that, when 1,1-diethoxyethane (XXXI) is treated with ozone at 20–60 °C, the corresponding hydroperoxide (XXXIII) and water are formed simultaneously with ethyl acetate (XXXII) and ethyl alcohol (Table 3):

$$CH_3CH(OC_2H_5)_2 + O_3 \begin{cases} \longrightarrow CH_3COOC_2H_5 + C_2H_5OH + O_2 \ ; \\ (XXXII) \\ \longrightarrow CH_3C(OOH)(OC_2H_5)_2 + H_2O \ . \\ (XXXIII) \end{cases}$$

With increase of temperature, the yield of the hydroperoxide and water with respect to the ozone consumed increases and at 50–60 °C reaches 30–40%. The presence of considerable amounts of hydroperoxides and water in the products of the ozonolysis of acetals is believed[32–35] to indicate the formation of radicals in the primary reaction of ozone with acetals.

The extent of formation of free radicals in the primary reaction between ozone and acetals has been estimated from the amount of hydroperoxides and water formed and also from the amount of ozone consumed under the conditions of non-chain formation of hydroperoxides.[32] It has been shown that the reactions involving free radicals are more characteristic of linear acetals (~50% at 60 °C), but, with decrease of temperature (<10 °C), the contribution of the radical pathway to the overall process becomes negligible.

Table 3. The influence of temperature on the composition of the products of the reaction of ozone with 1,1-diethoxyethane and 2-methyl-1,3-dioxolan at advanced stages of the reaction in the absence of a solvent.[32]

Reaction temperature, °C	Amount of initial compounds which have reacted, mmol		Yield of products, mmol			
	O_3	acetal	the ester (XXIX) or (XXXII)	C_2H_5OH	the hydroperoxide (XXX) or (XXXIII)	H_2O
			(XXXI)			
60	5.0	11.4	11.1	8.0	1.8	2.1
40	5.0	10.5	10.2	8.2	1.2	2.0
20	10.0	17.5	16.6	14.2	1.7	2.2
5	10.0	12.8	11.8	10.2	0.6	0.7
			(XXVIII)			
40	5.0	10.4	10.0	—	1.3	1.0
20	5.0	6.1	5.7	—	0.9	0.9
5	10.0	10.8	10.6	—	0	0

The rate of formation of free radicals in the reaction of ozone with 1,1-diethoxyethane has been investigated[35] using the results on the liquid-phase chain oxidation of the latter initiated by ozone. With continuous supply of an ozone–oxygen mixture to the reaction mixture, the initial rates of accumulation of the hydroperoxide (v_{AOOH}) and of consumption of ozone (v_{O_3}) were determined (Table 4).

Table 4. The rates of accumulation of the hydroperoxide (XXXIII) (v_{AOOH}), of the consumption of ozone (v_{O_3}), and of initiation (v_i) as a function of the ozone concentration in the gas mixture c_{O_3} in the reaction of ozone with the acetal (XXX) at T = 50 °C.[32,35]

$10^5 c_{O_3}$, M	$10^6 v_{O_3}$, mol litre^{-1} s^{-1}	$10^5 v_{AOOH}$, mol litre^{-1} s^{-1}	$10^6 v_i$, mol litre^{-1} s^{-1}	v_i/v_{O_3}
4.0	2.2	0.7	0.7	0.3
6.6	3.7	1.1	1.3	0.4
11.7	8.5	1.7	3.4	0.4
32.1	23.2	3.3	13.0	0.6
55.8	15.5	2.2	6.0	0.4
84.4	34.6	3.3	13.5	0.4

The rate v_{O_3} is directly proportional to a concentration of ozone in the gas mixture c_{O_3}, while the rates v_{AOOH} vary linearly with $v_{O_3}^{1/2}$ and $v_{AOOH}/v_{O_3} \geq 1$, which agrees with the mechanism of the radical process in which the hydroperoxide

appears in the step involving the abstraction of hydrogen from the substrate by the peroxy-radical:[10]

$$CH_3CH(OC_2H_5)_2 + O_2 \xrightarrow{k_1} CH_3\dot{C}(OC_2H_5)_2,$$
$$CH_3\dot{C}(OC_2H_5)_2 + O_2 \xrightarrow{k_2} CH_3C(O\dot{O})(OC_2H_5)_2,$$
$$CH_3C(O\dot{O})(OC_2H_5)_2 + CH_3CH(OC_2H_5)_2 \xrightarrow{k_3} CH_3C(OOH)(OC_2H_5)_2 + CH_3\dot{C}(OC_2H_5)_2,$$
$$2CH_3C(O\dot{O})(OC_2H_5)_2 \xrightarrow{k_4} \text{non-radical products.}$$

According to the mechanism proposed, the rate of formation of the hydroperoxide AOOH is given by the formula $v_{AOOH} = k_2 k_3^{-1/2}[AH]v_i^{1/2}$, where v_i is the rate of formation of radicals in the system in the stage involving initiation by the reaction of O_3 with the acetal.[35] These results (Table 4) made it possible to determine the ratio v_i/v_{O_3}, characterising the fraction of ozone consumed in the formation of free radicals, which is 0.45 ± 0.15. This permitted the hypothesis that the ozonolysis of acetals takes place simultaneously via molecular and radical pathways:[32,35]

$$CH_3CH(OC_2H_5)_2 + O_3 \text{ (AH)} \begin{cases} \xrightarrow{(a)} CH_3C(O_3H)(OC_2H_5)_2 \xrightarrow{-O_2} CH_3COOC_2H_5 + C_2H_5OH; \\ \xrightarrow{(b)} CH_3\dot{C}(OC_2H_5)_2 + O_2 + \dot{O}H \rightarrow \text{radicals;} \end{cases}$$
$$AH + \dot{O}H \rightarrow \dot{A} + H_2O; \quad \dot{A} + O_2 \rightarrow A\dot{O}_2; \quad A\dot{O}_2 + AH \rightarrow AOOH + \dot{A};$$
$$A\dot{O}_2 + A\dot{O}_2 \rightarrow \text{non-radical products.}$$

At temperatures below 10 °C the fraction of ozone consumed in the formation of free radicals [pathway (*b*)] is negligible and the reaction proceeds almost entirely via the formation of the unstable hydrotrioxide [pathway (*a*)]. With increase of temperature (above 10 °C), the fraction of ozone consumed in the formation of free radicals increases and conditions are created for oxidation by oxygen.

Table 5. The stoichiometry of the reaction of ozone with the dioxolans –R at 0 °C.[36]

R	Amount of acetal mmol		Amount of ozone absorbed, mmol	Solvent	α*
	initial	final			
CH_3	22.8	19.7	3.18	CH_2Cl_2	1.0
	17.4	13.8	3.46	ditto	0.94
	13.6	8.3	5.84	»	1.09
C_6H_5	16.2	11.5	5.00	»	1.06
	12.3	9.4	2.69	»	0.95
	9.2	4.4	4.70	»	1.01
p-$CH_3C_6H_4$	12.3	9.3	2.92	CCl_4	0.92
	9.1	2.6	6.68	ditto	1.03

*α is the ratio of the amount of ozone absorbed and the acetal which has been consumed.

IV. THE INFLUENCE OF THE STRUCTURE OF ACETALS AND THE CONDITIONS IN THEIR REACTION WITH OZONE ON THE RATE OF THE PROCESS

The stoichiometry of the reaction of ozone with acetals was first investigated in relation to 2-phenyl-1,3-dioxolan (I) at −78 °C in methyl acetate.[36] It was established that treatment of one mole of the acetal with ozone results in the formation of one mole of oxygen and one mole of glycol monoester. The results of further studies,[36] carried out in relation to 1,3-dioxolans substituted in 2-position at 0 °C, have shown that the stoichiometric ozone : acetal ratio is close to unity and is almost independent of the initial concentrations of the reactants (Tables 5 and 6).

When the reaction was carried out in the pure substrate (1,1-diethoxyethane or 2-methyl-1,3-dioxan) in the temperature range betwee −20° and 60 °C, it was found[32] that the stoichiometry of the reaction (O_3 : OH) changes from 1 : 1 (between −20° and 0 °C) to 1 : 2 (40–60 °C), which is associated with the occurrence of chain oxidation at temperatures ≥40 °C. On the other hand, when the concentrations of the acetal are close to those of ozone, the stoichiometric ratio of the reactants at 20 °C is close to unity.

Table 6. The stoichiometry of the reaction of ozone with the dioxolans –R in CCl_4 at 0 °C.[36]

R	c_{AH}, 10^{-4} M	c_1, 10^{-4} M	c_2, 10^{-4} M	$\alpha = \frac{c_1 - c_2}{c_{AH}}$
C_6H_5	7.1	9.4	2.3	1.00
	5.0	6.4	1.5	0.98
	3.7	5.8	2.0	1.03
CH_3	5.0	6.0	1.2	0.96
	3.0	6.2	3.3	0.97
	3.0	3.6	0.5	1.03

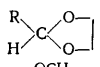
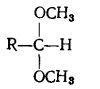
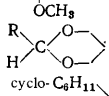
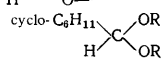
Notation: c_{AH} is the initial concentration of the acetal, c_1 the initial concentration of O_3, c_2 the final concentration of O_3.

This made it possible to investigate the reactivity of acetals with different structures in relation to ozone at 20 °C, the rate of consumption of ozone being followed spectrophotometrically. For all the compounds investigated, the kinetic O_3 consumption curves have the same form and, when [AH] ≫ [O_3], can be satisfactorily represented in a linear form by plotting $\ln [O_3]_0/[O_3]$ against time; under these conditions, ozone is consumed via a pseudounimolecular process with a rate constant $k' = v_{O_3}/[O_3]_0$.[18,29,31–37,40] With increase of the acetal concentration in solution, the rate constant k' increases linearly[32] and the initial rate of consumption of ozone obeys a second-order equation: $v_{O_3} = k[AH][O_3]$; the constant k reflects the overall reactivity of the acetal with respect to ozone and in the temperature range between −78° and 20 °C the process proceeds mainly via the molecular pathway.

The reactivity of 1,3-dioxacyclanes is determined by the ring size and the nature of the substituent at the C(2) carbon atom. The influence of ring size on the reactivity of acetals has been investigated.[18] Comparison of the bimolecular rate constants for the reactions of ozone with five-, seven-, and six-membered 1,3-dioxacyclanes has shown that the reactivity decreases in the sequence 1,3-dioxolan > 1,3-dioxepan > 1,3-dioxan. The dependence of $\lg(k_n/k_0)$ on n, where n (ring size) assumes values of 5, 6, and 7, is analogous to that for the solvolysis of chlorocycloalkanes and the thermal decomposition of cyclic diazoalkanes.[18] This enabled the authors to postulate the appearance in the transition state of a deficiency of electron density at the C(2) atom. The increase of reactivity after the introduction of alkyl and particularly phenyl substituents in the 2-position, which are capable of compensating for the decrease of electron density, has been explained[36] by the stabilisation of the positively charged species produced in which a p_z orbital is formed. The necessary effect is a maximum for 1,3-dioxans, since six-membered rings are less strained, resulting in an intermediate species which has a planar structure with the p_z orbital in

the same plane as the electron pairs of the oxygen atoms and the π orbitals of the phenyl substituent. The transition state in the case of seven- and particularly five-membered 1,3-dioxacyclanes largely deviates from the planar structure, as a result of which the conjugation with the p_z orbital is less effective.

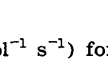
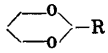
Table 7. Correlation between the rates of reaction with ozone and the Taft substituent constants.

Acetal	Solvent	T, °C	ρ	Correlation coefficient
	CCl_4	0	−1.16	0.995
	C_2H_5OAc	−78	−1.27	0.998
	C_2H_5OAc	−78	−1.58	0.980
	C_2H_5OAc	−78	−1.31	0.910

In order to determine the quantitative relations between the structure of the acetal and its reactivity towards ozone, a study has been made of the influence of substituents on the variation of the rate constants in series differing from one another only in the substituent. The experiments were performed at different temperatures (−78°, 0°, and 20 °C) and in solvents of different polarity (CCl_4,[36,37,40] ethyl acetate[37]).

Taft and Hammett inductive constants have been compared[36] with the relative rate constants for the reaction of ozone with 2-alkyl- or 2-aryl-1,3-dioxolans, which were determined by a competitive method at 0 °C in CCl_4, and also with the pseudo-unimolecular rate constants for the interaction of ozone with 2-alkyl-1,3-dioxans and 1,1-dimethoxyalkanes measured in ethyl acetates at −78 °C. These results showed that electron-donating substituents increase and electron-accepting substituents diminish the reactivity of acetals, the latter increasing by a factor of ~2 following the replacement of a non-polar solvent (hexane) by a polar solvent (ethyl acetate or acetic anhydride). The reaction paramters ρ, the absolute magnitude and sign of which characterises the change in the charge density in the reaction centre on passing from the ground to the transition state, are listed in Table 7. The increase in the negative value of ρ following the replacement of a non-polar solvent (CCl_4) by a more polar solvent (ethyl acetate) is noteworthy.

The quantitative relations between the structure of the acetals and their reactivity in the interaction with ozone in CCl_4 at 20 °C have been investigated taking into account the inductive (σ*) and steric (E_S) effects of the substituents.[40] For this purpose measurements were made of the rate constants for the reaction of ozone with linear formals and acetals having symmetrical and asymmetric structures, 2-alkyl-1,3-dioxolans and 2-alkyl-1,3-dioxans (Table 8). It has been established that the reactivities of the compounds investigated diminish in the sequence 1,3-dioxolans > 1,3-dioxans > 1,1-dialkoxyalkanes > dialkoxymethanes. The reaction rates constants correlate satisfactorily with the Taft inductive constant σ*; the sign of ρ is negative and its absolute magnitude varies in the sequence 1.0–1.6 (Table 9). The negative values of ρ in all the examples considered show that a partial positive charge is generated on the acetal carbon atom in the trantision state and the rate of ozonolysis is limited by the hydride transfer stage.[43,44] The characteristic influence of the nature of the solvent on the rate of the process, noted above, confirms the polarity of the transition state. In order to take into account simultaneously the influence of the inductive and steric effects[45] of the substituents

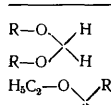
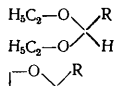
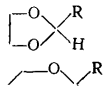
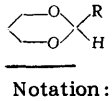
Table 8. The rate constants k (litre mol^{-1} s^{-1}) for reactions of the acetals $H_2C(OR)_2$, $R^1CH(OR^2)(OR^3)$, , and  with ozone in the liquid phase.[40]

No.	R	k	No.	R^1	k	No.	R^4	k	No.	R^5	k
(XXXIV)	C_2H_5	0.67	(XXVI)	H[a]	0.5	(XXXXV)	H	10.1	(XXXXIX)	H	0.90
(XXXV)	C_3H_7	0.69	(XXXXI)	H[b]	0.42	(XXVIII)	CH_3	22.8	(L)	CH_3	3.91
(XXXVI)	C_4H_9	0.78	(XXXI)	CH_3[c]	3.09	(XXXXVI)	iso-C_3H_7	40.1	(LI)	C_3H_7	9.01
(XXXVII)	iso-C_4H_9	0.91	(XXXXII)	C_3H_7[c]	4.01	(XXXXVII)	C_4H_9	49.2	(LII)	iso-C_3H_7	11.0
(XXXVIII)	C_5H_{11}	1.00	(XXXXIII)	C_4H_9[c]	4.56	(XXXXVIII)	iso-C_4H_9	61.7	(LIII)	C_4H_9	10.5
(XXIX)	iso-C_5H_{11}	0.79	(XXXXIV)	iso-C_3H_7[c]	5.47	(I)	C_6H_5	56.3	(LIV)	C_6H_5	19.5
(XXXX)	cyclo-C_6H_{11}	2.06									

Remarks: 25 °C; solvent—CCl_4; $[O_3] = 1.6 \times 10^{-4}$–$1.6 \times 10^{-3}$ M; [acetal] = 10^{-3}–10^{-2} M; [a] $R^2 = CH_3$, $R^3 = C_4H_9$; [b] $R^2 = CH_3$, R^3 = *iso*-C_5H_{11}; [c] $R^2 = R^3 = C_2H_5$.

on the rate of ozonolysis of acetals, relations of the type $\lg(k/k_0) = \rho\sigma^* + \delta E_S$ were investigated.[40] The two-parameter correlation (Table 9) describes the best reactivities of the compounds studied. The alkyl substituents R in the alcoholic component of the dialkoxymethanes do not manifest an appreciable steric effect (the steric constant for the reaction series is $\delta = -0.054$) because of their remoteness from the reaction centre, since the reactivities of compounds of this series are mainly determined by the inductive effect of the substituents ($\rho = -2.42$). The reactivities of 1,1-diethoxyalkanes, like those of dialkoxymethanes, are determined mainly by the inductive effect ($\rho = -2.30$). The positive sign of the steric constant δ for this reaction series is noteworthy, indicating a decrease of the reaction rate with increased bulk of the substituent at the reaction centre. The substituents in the reaction series involving the ozonolysis of 2-alkyl-1,3-dioxolans and 2-alkyl-1,3-dioxans (Table 8) exert an appreciable influence on the reactivity.[36,37] Analysis of the constants ρ and δ (Table 9) shows that the rate of the process is determined by the inductive and steric effects of the substituents and that the influence of the latter becomes decisive for 2-alkyl-1,3-dioxans. The observed difference between the five- and six-membered rings can be explained[40] by the conformational characteristics of the molecules considered. It is known that the introduction of a substituent into 1,3-dioxan fixes the chair confirmation,[46] while the C–H bond attacked is in a conformation favourable for reaction because its orientation is antiperiplanar relative to the orbitals of the free electron pairs of the oxygen atoms.[20] The five-membered ring does not have quite such a distinct conformational minimum[47,48] and the steric influence of the substituents in the 2-position is therefore smaller.

Table 9. The inductive (ρ) and steric (δ) constants for the reaction series involving the reaction of ozone with acetals.[40]

Compound	$\lg(k/k_0) = \rho\sigma^*$		$\lg(k/k_0) = \rho\sigma^* + \delta E_S$			
	ρ	r	ρ	δ	r	s
	−1.55	0.973	−2.42	−0.054	0.975	$0.4 \cdot 10^{-2}$
	−1.32	0.991	−2.30	0.38	0.998	$2.6 \cdot 10^{-4}$
	−1.02	0.937	0.68	−0.58	0.992	$0.4 \cdot 10^{-2}$
	−1.6	0.994	5.89	−2.92	0.990	$1.6 \cdot 10^{-2}$

Notation: r is the correlation coefficient and s the variance.

The activation parameters for the ozonolysis of linear and cyclic acetals determined in two investigations[36,37] are listed in Table 10. The high negative entropies of activation $\Delta S^{\neq}$ ($\Delta S^{\neq} = -141$ to -106 J mol^{-1} K^{-1} [36]) and the anomalous relation between the reactivities of linear acetals and the corresponding enthalpies of activation, namely the fact that the increase of the reactivity of the acetal is accompanied by an increase of the enthalpy of activation,[37] are noteworthy. It has also been established[37] that the enthalpy of activation $\Delta H^{\neq}$ and the entropy of activation $\Delta S^{\neq}$ are linked by a linear relation, so that a compensation effect is observed ($\Delta H^{\neq} = \beta\Delta S^{\neq} + h_0$; β is the isokinetic temperature and h_0 is a constant).[37] For linear acetals, the isokinetic temperature is much below the experimental temperature range and the reactivity is determined by the entropy factor.[37] Since, according to Deslongchamps et al.[22], linear acetals exist in a conformation which is inert towards ozone, in order to become reactive the acetal molecules must assume a favourable conformation[20] in which the C–H bond attacked is oriented antiperiplanarly relative to the unshared electron pairs of the oxygen atoms. For cyclic acetals, which exist in a favourable conformation,[22] β lies at higher temperatures than the working range[37] and the enthalpy factor determines the reactivity.

V. THE MECHANISM OF THE INTERACTION OF OZONE WITH ACETALS

The reaction of ozone with a saturated C–H bond can proceed via homolytic, concerted, and heterolytic mechanisms.[36,49,50]

The homolytic mechanism can operate in principle in several ways.[50] It can involve a chain reaction initiated by oxygen atoms, which are formed on reversible dissociation of ozone:

$$O_3 \rightleftarrows O_2 + O \quad (\Delta H = 107 \text{ kJ mol}^{-1} \text{ (Ref.50)}).$$

Analysis by Denisov[50] indicated a low probability of the occurrence of the chain reaction at reduced temperatures. This agrees with the finding that the initiating effect of ozone on the gas-phase oxidation of hydrocarbons is observed only at temperatures above 100 °C, where ozone decomposes at an appreciable rate.[50] In the liquid phase at moderate temperatures the radicals can be generated via a bimolecular reaction. However, the mechanism involving abstraction of a hydrogen atom is believed to be unlikely in view of the high endothermicity of the reaction:

$$RH + O_3 \rightarrow R^{\cdot} + HO_3^{\cdot} - q \quad (q = Q_{R-H} - 255 \text{ [56]}),$$

which does not agree with experimental data.[36] For example, $Q_{R-H} \cong 340$ kJ mol^{-1} [10] and $q \cong 85$ kJ mol^{-1} for 1,3-dioxacyclanes, while the activation energy for the ozonolysis of acetals varies in the range 22–35 kJ mol^{-1}.[36]

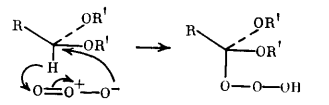
The formation of radicals is a result of the attack by ozone on the C and H atoms in the C–H bond, while the mechanisms $RH + O_3 \rightarrow R\dot{O} + H\dot{O}_2$ [54,55] and $RH + O_3 \rightarrow R\dot{O}_2 + H\dot{O}$ [57,58] are also unlikely, because it is known that this should lead to a high activation energy (above 100 kJ mol^{-1}) and to a high negative entropy of activation. Denisov pointed out[50] that the reaction

$$RH + O_3 \rightarrow R^{\cdot} + HO^{\cdot} + O_2 - q \quad (q = Q_{R-H} - 320 \text{ kJ mol}^{-1} \text{ (Refs.59, 60)})$$

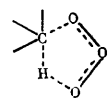
is thermodynamically the most favourable among homolytic reactions. For example, the endothermicity of this reaction for 1,3-dioxacyclanes is only 20 kJ mol^{-1}, which agrees well with the activation energy $E = 22$–35 kJ mol^{-1} [36] (for endothermic reactions, $E > |q|$ [50]). The above analysis shows that the homolytic interaction of ozone with a saturated C–H bond can proceed at the experimentally observed rate at elevated temperatures, provided that the energy of the C–H bond attacked does not exceed 340 kJ mol^{-1}. This is consistent with the finding that, under conditions suitable for a chain reaction, namely [RH] > 5 M and T > 50 °C, ozone initiates the chain oxidation of acetals.[32,35] Below 0 °C, the probability of the formation of free radicals as a result of the primary reaction of ozone with acetals is low.

The observed high rates of reaction of ozone with acetals at reduced temperatures (Table 1) indicate the possibility of the concerted and heterolytic reaction mechanisms.

The concerted mechanism involving the 1,3-dipolar insertion of ozone in the C–H bond with formation of an intermediate hydrotrioxide can be represented by the following scheme accordingly to Nagia and Benson:[49]



In the case of a concerted reaction, the insertion of O_3 in the C–H bond takes place tentatively via a five-membered cyclic transition state of the following form:[49]



Calculations have shown that the formation of the cyclic transition state, involving a marked extension of the C–H bond and a considerable change in the O–O–O valence angle in the ozone molecule, leads to a high activation energy (above 100 kJ mol^{-1}) [51] and to a high negative entropy of activation.[50] Consequently the mechanism involving the 1,3-dipolar insertion of ozone is also unlikely.

The primary reaction of ozone with an acetal apparently takes place heterolytically via the transfer of a hydride ion to the O_3 molecule with formation of a close ion pair in a solvent cage, which then recombines to form the hydrotrioxide:[36,49]

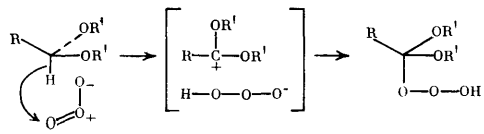
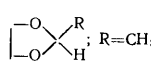
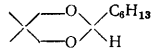


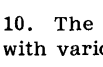
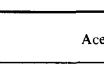
Table 10. The activation parameters for the reactions of ozone with various acetals.

No.	Acetal	Solvent	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
(XXVIII)	 R=CH$_3$	CCl_4	22.6±2.9	−141±10
(I)	R=C$_6$H$_5$	CCl_4	24.9±0.4	−125±2
(III)		Hexane	34.3±3.5	−106±17
(III)	ditto	C_2H_5OAc	33.2±2.5	−106±12
(LV)	iso-C$_3$H$_7$–C(OCH$_3$)$_2$–H	C_2H_5OAc	37.4±0.7	−110±3
(VII)	C$_6$H$_{17}$–C(OCH$_3$)$_2$–H	C_2H_5OAc	35.2±1.6	−121±7

Under these conditions, a partial positive charge is generated on the acetal carbon atom in the transition state. The validity of this hypothesis is confirmed by the results of a study of the reactivity of acetals using the Taft correlation equation (Table 9),[36,40] the study of the influence of the ring size and of the nature of the substituent at the acetal carbon atom on the reactivity of acetals,[18] and the high negative activation entropies $\Delta S^{\neq}$ for the ozonolysis of acetals (Table 10).[36] It is known[52] that the appearance of a pair of charges in the transition state leads to a significant decrease of the entropy and $\Delta S^{\neq}$ can reach −120 J mol^{-1} K^{-1}.[52] The results of Benson's thermochemical calculations[49] support the heterolytic reaction pathway.

Additional data concerning the primary reaction of ozone with acetals have been obtained in a study of the kinetic isotope effect (KIE).[53] Experiments on the reaction of ozone with the deuterio-acetals of acetaldehyde, benzaldehyde, and formaldehyde demonstrate unambiguously that in acetals the attack by ozone is directed to the C–H bond adjoining two heteroatoms (Table 11). Estimation of the absolute values of the KIE and their comparison with the known $\Delta S^{\neq}$ for the corresponding acetals[36] make it possible to infer the degree of charge separation in the transition state. Since the KIE is manifested when the hydride ion has been partially transferred to the ozone molecule in the transition state, its magnitude increases with increase of the degree of transfer and reaches its maximum value ($k_H/k_D \cong 6.9$ at 25 °C [52]) for complete symmetry of the transition state when the C–H bond ruptured and the H–O bond formed have similar strengths.[52] Consequently, the increase of the KIE on passing from formals and linear acetals to cyclic acetals (Table 11), accompanied by a decrease of the corresponding $\Delta S^{\neq}$, indicates an increase in the degree if charge separation in the transition state of the reaction between acetals and ozone.

Table 11. The kinetic isotope effects and entropies of activation in the reactions of ozone with acetals at 20 °C [53] ($v_{O_3} = kc_{ac}c_{O_3}$).

Compound	k, litre mol^{-1} s^{-1}		k_H/k_D	$\Delta S^{\neq}$, J mol^{-1} K^{-1} (X = H)
	X=H	X=D		
	22.8	4.8	4.9	−141
	53.6	12.4	4.3	−125
$CX_3CX(OC_2H_7)_2$	2.0	0.55	3.6	−104
	1.3	0.4	3.0	−94.3
	5.6	1.9	2.9	—
$X_2C(OC_3H_7)_2$	0.60	0.28	2.1	—

Thus analysis of data on the composition of the products of the reactions of ozone with acetals,[20,29,32] the stoichiometry of the reaction,[32,36] and the influence of the nature of the substituents and the structure of the acetals on their reactivity over a wide temperature range (between −78° and 60 °C),[18,40] allowance for the polarity of the medium,[37] and analysis of the activation parameters for the process and of the KIE [36,53] permit the conclusion that the nature of the primary reaction of ozone with acetals is complex. At reduced temperatures the process proceeds via a heterolytic mechanism with transfer of the hydride ion and the formation of an ion pair in a solvent cage: its recombination leads to an intermediate highly unstable hydrotrioxide whose decomposition leads to the formation of the observed reaction products.

Under these conditions (between −70° and 20 °C), the probability of the homolytic reaction pathway is insignificant. With increase of temperature (>20 °C), the fraction of ozone consumed in the formation of free radicals increases, reaching ~40–50% at 50 °C.[32,35]

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