Acetal Hydrotrioxides†

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Summary Low-temperature ozonation of aliphatic and aromatic acetals leads to oxygen rich intermediates, the acetal hydrotrioxides (**1**)—(**3**), the n.m.r. spectra of which show two OOOH absorptions at *ca.* δ 13; decomposition of these compounds which affords among other products, singlet oxygen, involves non-radical and radical processes.

EXPERIMENTAL[1] and theoretical[2] evidence has been given in recent years for the existence of polyoxides of the type RO_nR (R = H, alkyl; n = 3,4). Much less is known about the hydrotrioxides, RO_3H, which have been proposed as unstable intermediates in ozonation of various organic compounds.[3] It was only recently, however, that Murray *et al.* reported the first spectroscopic evidence for their existence.[3]

As a part of our interest in polyoxides we report additional experimental evidence for the existence of hydrotrioxides in the low temperature ozonation of acetals. Deslongchamps *et al.* have already proposed these species as one of the possible intermediates in these reactions.[4]

TABLE. Kinetic and activation parameters for the decomposition of acetal hydrotrioxides.

Hydrotrioxide	Solvent	Temp/°C[a]	k_1/s^{-1}[b]	E_a/kcal mol^{-1}[c]	log *A*	δ OOOH (Me_4Si)[d] −55 °C	
(**1a**)	Neat	−10	$2{\cdot}7 \times 10^{-2}$			12·8	13·3 (1:2·5)
"	Et_2O[e]	−20	$8{\cdot}5 \times 10^{-3}$	16·1	11·8	12·8	13·2 (1:2)
"	"	−10	$2{\cdot}9 \times 10^{-2}$				
"	CH_2Cl_2[e]	−10	$4{\cdot}0 \times 10^{-2}$				
(**1b**)	Neat	−20	$3{\cdot}7 \times 10^{-2}$	14·5	11·1	12·8	13·2 (1:1·5)
"	"	−10	$1{\cdot}1 \times 10^{-1}$				
"	Et_2O[e]	−20	$2{\cdot}8 \times 10^{-2}$	13·2	9·6	12·8	13·2 (1:1)
"	"	−10	$7{\cdot}6 \times 10^{-2}$				
(**2**)	Et_2O[e]	−40	$1{\cdot}6 \times 10^{-2}$	14·9	12·2	13·10	13·16 (1·5:1)[f]
"	"	−30	$6{\cdot}6 \times 10^{-2}$				
(**3**)	Et_2O[e]	−40	$1{\cdot}2 \times 10^{-2}$	19·0	15·8	12·5	12·8 (1:2·5)
"	"	−30	$6{\cdot}5 \times 10^{-2}$				

[a] The temperature range was dictated by both solubility problems and fast decomposition with gas evolution. [b] Standard deviations ±7%. [c] In view of the complexity of the decomposition, which proceeds by several simultaneous first-order pathways, the significance of the activation parameters is relatively small. [d] Simultaneous appearance of the OOOH absorption and disappearance of the O–CH–O absorption was observed during ozonation of all the acetals investigated. [e] Acetal (20 mmol), 30%; Et_2O, 70% (by wt.). Ozonation was performed with an ozone–oxygen stream (*ca.* 0·2 mmol min^{-1}) aliphatic acetals, 5 h at −55 to −50 °C; aromatic acetals, 2 h). [f] Another absorption of low intensity at δ 12·8 (absent in CH_2Cl_2) has also been observed.

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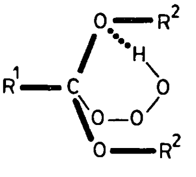
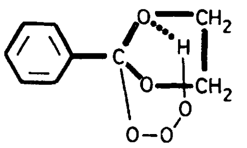
The reaction of ozone (ozone–oxygen or ozone–nitrogen mixture) with acetals either neat (aliphatic acetals) or in diethyl ether or methylene chloride, below −50 °C, produces unstable oxygen-rich intermediates, the n.m.r. spectra of which show two absorptions at δ *ca.* 13 downfield from Me_4Si. Since their position does not change much with dilution they are tentatively assigned to the OOOH absorptions of the intramolecularly hydrogen bonded six-membered rings of the hydrotrioxides of types (**1**), (**2**), and (**3**). The n.m.r. data, along with kinetic and activation parameters for the first-order decay of the OOOH absorptions, are in the Table.



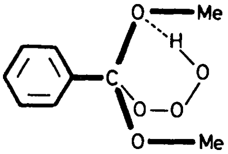
(1)

a; R^1 = Me R^2 = Me

b; R^1 = Me R^2 = Et



(2)

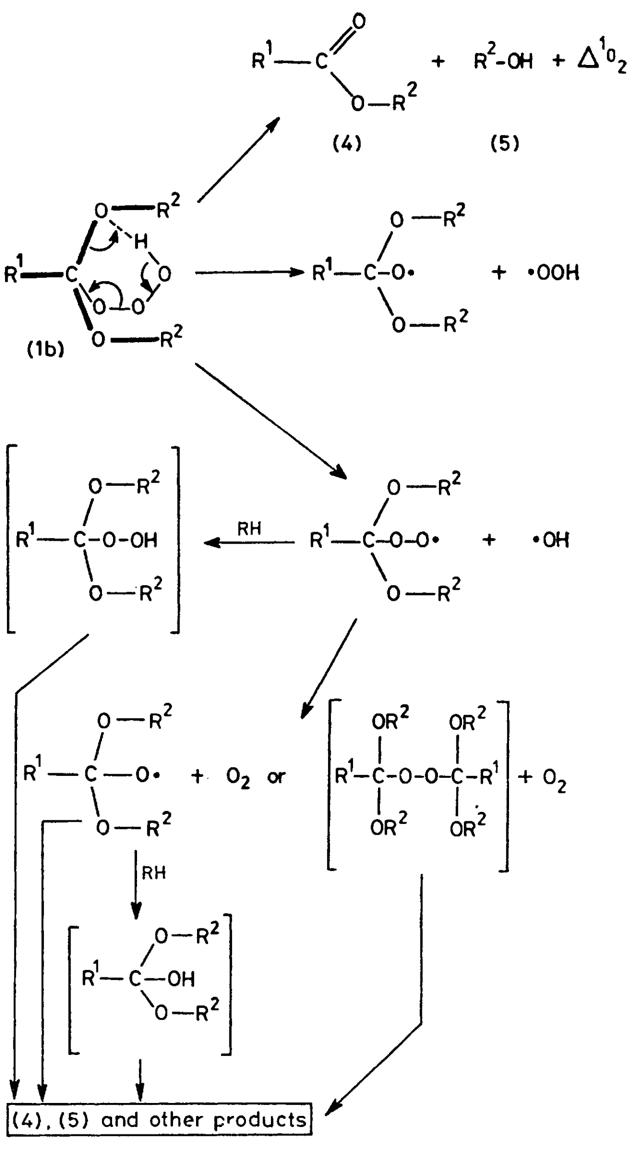


(3)

While the origin of the two absorptions for the OOOH protons remains uncertain, it is interesting that Murray *et al.* made a similar observation in the case of 2-methyltetrahydrofuran hydrotrioxide. Both peaks show a tendency to merging and broadening at higher temperatures. A characteristic feature is the small splitting for (**2**), which is absent for the *para*-methyl analogue. We believe that this splitting might be due to the presence of two conformations of the acyclic acetal hydrotrioxides, resulting from the non-equivalency of the two acetal oxygens with respect to the OH group.[5] The R^2 groups might change their conformational character without cleavage of the intramolecular hydrogen bond. The conformational changes (chair–boat) of the six-membered ring, involving three oxygen atoms, with the R substituent on the acetal oxygen, axial or equatorial, might also be a valid explanation. It has already been suggested, however, that the five-membered acetal ring in (**2**) is nearly planar thus not allowing appreciable conformational changes.[5]

The effect of the solvent on the rate of decomposition of aliphatic acetal hydrotrioxides is rather small under the conditions investigated. Comparable rate constants were obtained by studying the decomposition of (**1a**) in the parent acetal, diethyl ether, and methylene chloride, respectively. The activation parameters in the Table are in good qualitative agreement with those reported for other polyoxides.

All the hydrotrioxides investigated decompose in the temperature range −40 to −10 °C to produce singlet oxygen. *Ca.* 55—60% of the absorbed ozone was available to react with 1,3-diphenylisobenzofuran in the case of (**1b**), 75—80% in the case of (**2**), and 45—50% in the case of (**3**), respectively. The yield of hydrotrioxides (**2**) and (**3**) was estimated by n.m.r. spectroscopy to be 70—85%. A detailed study of the decomposition products of (**1b**) (ozonation in an ozone–nitrogen stream at −55 °C[6]; g.l.c., Porapak Q columns, 80—170 °C) showed ethyl acetate (0·80—0·85 mol per mol of absorbed ozone) and ethanol (0·70—0·75 mol) as well as water, acetaldehyde, acetic acid, ethyl formate, diethyl carbonate, and small but definite amounts of two gases (presumably methane and ethane). Two, as yet not completely identified, peroxides were also separated from the decomposition mixture on preparative silica plates. N.m.r. and i.r. spectroscopic evidence indicates that they are alkyl hydroperoxide and dialkyl peroxide, respectively. Small amounts of hydrogen peroxide have also been detected.



Scheme

On the basis of these results we conclude that the formation of a large part of the ethyl acetate and ethanol, together with singlet oxygen, can be tentatively ascribed to a non-radical decomposition of the hydrotrioxide (**1b**), while the presence of the other products in the decomposition mixture suggests an alternative free-radical decomposition process as shown in the Scheme.

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