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Radical-Chain Reactions of Acetals in Solution

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Experimental results on the liquid-phase radical-chain reactions of acetals are summarised. Factors influencing the rate of formation, structure, and properties of free radicals generated from cyclic and linear acetals are discussed. Attention is paid mainly to the kinetics and the mechanism of the reactions of mono- and di-alkoxyalkyl radicals in solution. The relation between the structure of acetals and their reactivity towards various radicals is examined. Data are given illustrating the possibility of using homolytic liquid-phase reactions of acetals in organic synthesis. A list of 77 references is included.

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I. INTRODUCTION

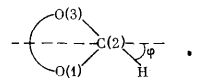
During the last 10–15 years much interesting information has been obtained on the chemistry of homolytic liquid-phase reactions of 1,3-dioxacyclanes, which has been surveyed in part[1]. This field has since been widely developed in the chemistry of acetals, and the results surveyed[1] no longer reflect the progress made in the study of radical–chain reactions of 1,1-dialkoxyalkanes, 1,3-dioxacyclanes, and related compounds.

Acetals and their hetero-analogues are successfully employed in the synthesis of various organic compounds, and are also widely used as solvents, plasticisers for polymeric materials, etc. Furthermore, linear and cyclic acetals often serve as subjects for the study of theoretical problems in organic chemistry connected with the interaction of two oxygen atoms separated by a carbon atom. The urgency of systematising and generalising data on radical reactions of acetals in the liquid phase is due to the possibility of their forming the basis of industrial processes for obtaining esters, halogenohydrin ethers, telomeric acetals, etc. from inexpensive and accessible petrochemical products.

Among the tasks of the present Review are to discuss research results on radical–chain reactions of acetals, to analyse the factors determining their reactivity, and to assess the prospects for using homolytic reactions of acetals for organic synthesis. Since an immense quantity of experimental results have been obtained on the liquid-phase oxidation of oxygen-containing organic compounds, in particular acetals, and require separate systematisation and discussion, they will not be considered in the present Review.

II. STRUCTURE OF RADICALS GENERATED FROM CYCLIC AND LINEAR ACETALS

The formation and the three-dimensional structure of mono- and di-alkoxyalkyl radicals generated from linear and cyclic acetals have been investigated by electron spin resonance spectroscopy[2–13]. Analysis of the hyperfine coupling constants of the unpaired electron with an α-hydrogen atom $a(\alpha\text{-H})$ has established[2–4,11] that in cyclic systems the deviation of the bonds of the tervalent carbon atom in dialkoxyalkyl radicals from the planar structure characteristic of alkyl and cycloalkyl radicals increases as the ring becomes smaller. The same effect has been found[13] in calculations by the extended Hückel method of the angles ϕ of distortion of the C–H bond from the plane formed by the $O_{(1)}$–$C_{(2)}$ and $C_{(2)}$–$O_{(3)}$ bonds in cyclic mono- and di-alkoxyalkyl radicals



In the 1,3-dioxacyclohex-2-yl radical the angle ϕ should be 15°, but in 1,3-dioxacyclopent-2-yl 20–25°. The dependence of $a(\alpha\text{-H})$ on ϕ can be approximated by the linear equation $a(\alpha\text{-H}) = -23.1 + 1.44\phi$.[13]

A relation has been identified[8,11] between the structure and the selectivity of formation z of cyclic dialkoxyalkyl radicals (Table 1):

$$z = \left(\frac{[N]}{[M]}\right)_{\dot{N}H_2} / \left(\frac{[N]}{[M]}\right)_{\dot{O}H},$$

where N is the dialkoxyalkyl radical, M is an alkoxyalkyl radical, and $([N]/[M])_{NH_2\cdot}$ and $([N]/[M])_{HO\cdot}$ are the concentration ratios of di- and mono-alkoxyalkyl radicals formed from acetals by the action of $\cdot NH_2$ and HO· radicals respectively.

When an acetal is attacked by different types of radicals (hydroxyl ·OH and aminyl $\cdot NH_2$), preferential formation of the 1,3-dioxacycloalk-2-yl radicals is observed[8] in both cases (Table 1). This indicates that a hydrogen atom is abstracted from the methylene or methine group between the two oxygen atoms more readily than from any other positions in the molecule. Introduction of a methyl group at position 2 or 4 facilitates formation of the corresponding di- and mono-alkoxycycloalkyl radicals (Table 1), which is more clearly evident with aminyl radicals[14].

Examination of the behaviour of cyclic formals reveals the largest difference between rate constants of homolytic cleavage of non-equivalent carbon–hydrogen bonds in 1,3-dioxolan (Table 1). Divergence from a planar structure is about the same in radicals (IX), (XIX), and (XXIV), and their rates of formation by the action of hydroxyl and aminyl radicals should not differ significantly. However, whereas radicals (XVIII) and (XXIII) give negative values of $a(\alpha\text{-H})$, −1.0 and −4.2 oersteds respectively[2], (VIII) gives $a(\alpha\text{-H}) =$ 21.5 oersteds[2,8]: i.e. the orbital of the unpaired electron is more involved in "partial" sp^3-hybridisation in (VIII). On

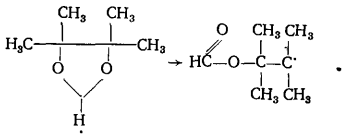
Table 1. Spectroscopic constants, relative steady-state concentrations ε, and selectivity of formation z of radicals generated from 1,3-dioxacyclanes (I)–(VII) by the action of HO· and H_2N· radicals[8].

No.	1,3-Dioxacyclane (DH) formula	No.	Radicals (D·) formula	$a(\alpha\text{-H})$, oersteds	$a(\beta\text{-H})$, oersteds	$a(\gamma\text{-H})$, oersteds	g-Factor	g-Factor ȮH	g-Factor ṄH₂	$z=\left(\frac{N}{M}\right)_{\dot{N}H}/\left(\frac{N}{M}\right)_{\dot{O}H}$
(I)	$OCH_2CH_2OCH_2$	VIII	$OCH_2CH_2O\dot{C}H$	21.5 (d)	—	1.4 (q)	2.0032	2.0	5.0	
		IX	$O\dot{C}HCH_2OCH_2$	11.4 (d)	27.2 (t)	1.5 (t)	2.0032	1.0	1.0	2.5
(II)	$OCH(CH_3)CH_2OCH_2$	X	$OCH(CH_3)CH_2O\dot{C}H$	22.0 (d)	—	1.5 (q)	2.0032	3.0	5.0	
		XI	$O\dot{C}(CH_3)CH_2OCH_2$	—	19.8 (q)	1.0 (t)	2.0030	1.5	1.0	2.5
		XII	$OCH(CH_3)\dot{C}HOCH_2$	11.4 (d)	26.4 (q)	1.4 (m)	2.0032	1.0	*	
(III)	$OCH(CH_3)CH_2OCHCH_3$	XIII	$OCH(CH_3)CH_2O\dot{C}CH_3$	—	13.5 (q) 22.5 (q)	1.0 (m)	2.0030	4.0	5.0	
		XIV	$O\dot{C}(CH_3)CH_2OCHCH_3$	—	23.5 (q)	—	2.0030	2.0	1.0	2.5
		XV	$OCH(CH_3)\dot{C}HOCHCH_3$	11.4 (d)	28.7 (q)	—	2.0030	1.0	*	
(IV)	$OCH(CH_3)CH(CH_3)OCCH_2CH_2CH_2CH_2$	XVI	$O\dot{C}(CH_3)CH(CH_3)OCCH_2(CH_2)_2CH_2$	—	20.5 (q) 28.0 (q)	—	2.0031	1.0	3.0	3.0
		XVII	$OCH(CH_3)CH(CH_3)O\dot{C}CH(CH_2)_2CH_2$	21.7 (d)	37.0 (q)	0.5	2.0029	1.0	1.0	
(V)	$OC(CH_3)_2CH_2CH_2OCH_2$	XVIII	$OC(CH_3)_2CH_2CH_2O\dot{C}H$	1.0 (d)	—	—	2.0030	2.0	4.0	
		XIX	$OC(CH_3)_2CH_2\dot{C}HOCH_2$	16.6 (d)	47.5 (t)	1.6 (t)	2.0031	1.0	1.0	2.0
(VI)	$OCH(CH_3)CH_2CH_2OCHCH_3$	XX	$OCH(CH_3)CH_2CH_2O\dot{C}CH_3$	—	14.2 (q)	—	2.0029	3.0	6.0	
		XXI	$O\dot{C}(CH_3)CH_2CH_2OCHCH_3$	—	49.5 (t) 23.2 (q)	0.5 (d)	2.0030	1.0	1.0	2.0
		XXII	$OCH(CH_3)CH_2\dot{C}HOCHCH_3$	10.4 (d)	31.2 (t)	0.5 (d)	2.0031	1.0	*	
(VII)	$OCH_2CH_2CH_2CH_2OCH_2$	XXIII	$OCH_2CH_2CH_2CH_2O\dot{C}H$	4.2 (d)	—	1.0 (m)	2.0030	1.0	2.0	1.3
		XXVI	$O\dot{C}HCH_2CH_2CH_2OCH_2$	17.2 (d)	25.2 (t)	—	2.0028	1.0	1.5	

Note. Here d = doublet, m = multiplet, q = quintet, and t = triplet. The respective sources of HO· and H_2O· radicals were[8,11] the $Ti^{III} + H_2O_2$ and $Ti^{III} + NH_2OH$ redox systems.
*Signal of radical in e.s.r. spectrum at noise level.

this basis it was suggested[8] that attainment of the transition state in the abstraction of a hydrogen atom by active hydroxyl and aminyl radicals with homolysis of the $C_{(2)}$–H bond occurs more readily in compound (I) than in (V) and (VII). This provided a satisfactory explanation of the decrease in selectivity z on passing from five-membered to six- and seven-membered 1,3-dioxacyclanes (z respectively 2.5, 2, and 1.3).[8] This effect is also responsible for a somewhat greater selectivity ($z \cong 3$) of formation of the monoalkoxyalkyl radical (XVI) than of the cycloalkyl radical (XVII) in the case of the acetal (VI), when the differences in strength of carbon–hydrogen bonds and in geometry of the resulting radicals are very great in the 1,3-dioxacyclane and cyclopentane fragments.

The e.s.r. spectra of the acetals investigated (I)–(VII) revealed no signals that could have been assigned to acyclic acyloxyalkyl radicals[2,3,8]. At 30–50 °C and also when rearrangement of cyclic dialkoxyalkyl radicals is accompanied by the formation of tertiary acyloxyalkyl radicals, however, signals from the latter are observed in the e.s.r. spectra[11]:



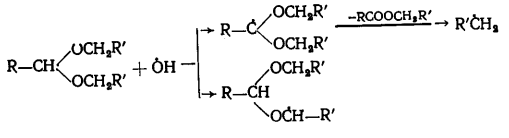
Similar observations have been made[12] on radicals generated by the photodecomposition of t-butyl peroxide. Hence cyclic dialkoxyalkyl radicals are not converted into linear acyloxyalkyl radicals at relatively low temperatures. Such rearrangement becomes appreciable above 60 °C, and causes formation of the corresponding acyclic products in the isomerisation, addition, and telomerisation of cyclic acetals[1].

Table 2. Spectroscopic constants and relative contents of radicals generated from 1,1-dialkoxyalkanes by the action of HO· and H_2N· radicals[9].

1,1-Dialkoxyalkane No.	1,1-Dialkoxyalkane formula	Radicals No.	Radicals formula	$a(\alpha\text{-H})$, oersteds	$a(\beta\text{-H})$, oersteds	$a(\gamma\text{-H})$, oersteds	[N]:[Alk], [M]:[Alk], [Alk]*
(XXV)	$CH_2(OCH_3)_2$	(XXXI)	$H\dot{C}(OCH_3)_2$	13.4 (d)	—	0.9 (sp)	2.0
		(XXXII)	$CH_2(OCH_3)O\dot{C}H_2$	17.9 (t)	—	0.9 (t)	9.0
		(XXXIII)	$\dot{C}H_3$	23.0 (q)	—	—	1.0
(XXVI)	$CH_2(OC_2H_5)_2$	(XXXIV)	$H\dot{C}(OC_2H_5)_2$	11.7 (d)	—	0.8 (m)	2.0
		(XXXV)	$CH_2(OC_2H_5)OCH_2\dot{C}H_2$	14.7 (d)	23.0 (d)	0.8 (t)	2.0
		(XXXVI)	$CH_3\dot{C}H_2$	22.4 (t)	26.9 (d)	—	1.0
(XXVII)	$CH_2(OC_3H_7)_2$	(XXXVII)	$\dot{C}H(OC_3H_7)_2$	10.5 (d)	—	0.8 (m)	1.0
		(XXXVIII)	$CH_2(OC_3H_7)O\dot{C}HCH_2CH_3$	14.4 (d)	21.0 (t)	0.8 (m)	14.0
		(XXXIX)	$CH_3CH_2\dot{C}H_2$	22.0 (t)	27.9 (t)	0.8 (m)	1.0
(XXVIII)	$CH_2[OCH(CH_3)_2]_2$	(XL)	$H\dot{C}[OCH(CH_3)_2]_2$	10.6 (d)	—	0.7 (t)	0.5
		(XLI)	$CH_2[OCH(CH_3)_2]O\dot{C}(CH_3)CH_3$	—	20.8 (m)	0.7 (t)	2.3
		(XLII)	$CH_3\dot{C}HCH_3$	21.5 (d)	24.9 (m)	—	1.0
(XXIX)	$CH_3CH(OCH_3)_2$	(XLIII)	$CH_3\dot{C}(OCH_3)_2$	—	14.8 (d)	0.8 (sp)	2.0
		(XLIV)	$CH_3C(OCH_3)O\dot{C}H_2$	17.5 (t)	—	0.5 (d)	14.0
		(XLV)	$\dot{C}H_3$	23.0 (q)	—	—	1.0
(XXX)	$CH_3CH(OC_3H_7)_2$	(XLVI)	$CH_3\dot{C}(OC_3H_7)_2$	—	14.2 (d)	0.8 (m)	12.0
		(XLVII)	$CH_3CH(OC_3H_7)O\dot{C}HCH_2CH_3$	14.4 (t)	20.8 (t)	0.8 (m)	12.0
		(XLVIII)	$CH_3CH_2\dot{C}H_2$	20.0 (t)	27.9 (t)	0.8 (m)	1.0

*Concentrations of di- and mono-alkoxyalkyl radicals N and M relative to concentration of alkyl radicals Alk.

Study of the structure and selectivity of formation of radicals from 1,1-dialkoxyalkanes (linear acetals) had established[8] simultaneous formation of mono- and di-alkoxyalkyl together with alkyl radicals by the action of hydroxyl radicals (Table 2). These last result from breakdown of relatively unstable linear dialkoxyalkyl radicals[12]:



Selectivity of formation of dialkoxyalkyl radicals increases somewhat on passing from formals (XXV)–(XXVIII) to acetals (XXIX) and (XXX). On treatment of diethoxymethane (XXVI) with the less active (than hydroxyl) aminyl radicals the selectivity of formation of diethoxymethyl radicals is approximately doubled[9]. Among the formals (XXV)–(XXVIII) increase in size and branching of the alkoxy-substituent is accompanied by an increase in relative e.s.r. signal intensity of the alkyl radicals (XXXIII), (XXXVI), (XXXIX), and (XLII), which is explained by enhancement of their stability. The concentration of alkyl radicals generated from the acetals (XXIX) and (XXX) is lower than that from the formals (XXV) and (XXVII) (Table 2), owing to the lower rate of rearrangement of tertiary than of secondary dialkoxyalkyl radicals, which is also indicated by other results[13].

III. REACTIVITY OF ACETALS TOWARDS VARIOUS RADICALS

Published data on the activity of acetals in reactions with different kinds of radicals have been obtained mainly by methods of competing reactions. The relative activities of linear, cyclic, and cyclolinear acetals towards t-butoxy-radicals have been studied[15–17], and the partial contributions by individual hydrocarbon groups determined. Table 3 summarises values of the ratio k_a/k_d for linear[15], cyclolinear[16], and cyclic[17] acetals, where k_a ($M^{-1}\ s^{-1}$) is the rate constant for abstraction of a hydrogen atom from a substrate molecule by a t-butoxy-radical

$$\text{t-BuO}^{\cdot} + QH \xrightarrow{k_a} \text{t-BuOH} + Q^{\cdot}$$

and k_d (s^{-1}) the rate constant of fragmentation of the t-butoxy-radical

$$\text{t-BuO}^{\cdot} \xrightarrow{k_d} CH_3COCH_3 + CH_3^{\cdot}\ .$$

Additive analysis of values for the ratio in Refs. 15–17 has shown that the relative partial rate constant for abstraction of a hydrogen atom from a methylene group in a hydrocarbon chain at 130 °C is 0.07–0.15 M^{-1}, and that for the methylene group $OCH(CH_3)$ is ~2.6 M^{-1}. The activation energy of detachment of a hydrogen atom from 1,1-dialkoxyalkanes by t-butoxy-radicals has been estimated[15] as lying in the range 6.5–8.5 kcal $mole^{-1}$.

Differences in reactivity between cyclolinear 2-alkoxyoxans and 2-alkoxyoxolans—(XCII)–(XCVI), (XCIX)–(CII) and (CIII)–(CVI)—are determined by the partial contributions of the alkoxyl substituents[16]. Partial contributions at 130 °C to k_a/k_d are approximately[16] 1.7, 2.8–3.0, and 0.3 M^{-1} for oxan-2-yloxy, oxolan-2-yloxy, and methoxy respectively.

Five-membered are more active than the corresponding six-membered 2-alkoxyoxacyclanes. Ring size has a similar influence among cyclic ethers, cyclic acetals[17], and their hetero-analogues[11]. The activation energy for abstraction of a hydrogen atom from 2-alkoxyoxacycloalkanes has been given[16] as ~7.0 kcal $mole^{-1}$. Abstraction of a hydrogen atom from a carbon atom adjacent to two oxygen atoms takes place most selectively[15–17] in cyclic and less selectively in linear acetals (Table 3); 2-alkoxyoxacycloalkanes occupy an intermediate position.

Table 3. Values of k_a/k_d for acetals (chlorobenzene solutions at 130 °C).[15-17]

No.	Acetal formula	k_a/k_d, M^{-1}	No.	Acetal formula	k_a/k_d, M^{-1}
(XXVII)	$(C_3H_7O)_2CH_2$	2.3	(I)	$CH_2CH_2OCH_2O$	5.2
(XLIX)	$(C_4H_9O)_2CH_2$	2.6	(LXXVI)	$CH_2CH_2OCH(CH_3)O$	6.1
(L)	$(C_5H_{11}O)_2CH_2$	2.8	(LXXVII)	$CH_2CH_2OCH[CH(CH_3)_2]O$	6.3
(LI)	(cyclo-$C_6H_{11}O)_2CH_2$	5.3	(LXXVIII)	$CH_2CH_2OCH(C_6H_{11})O$	6.4
(XXIX)	$(CH_3O)_2CHCH_3$	3.0	(LXXIX)	$CH_2CH_2OCH(C_6H_5)O$	6.6
(LII)	$(C_2H_5O)_2CHCH_3$	3.2	(LXXX)	$CH_2CH_2CH_2OCH_2O$	1.3
(XXX)	$(C_3H_7O)_2CHCH_3$	3.4	(LXXXI)	$CH_2CH_2CH_2OCH(CH_3)O$	2.7
(LIII)	$(C_4H_9O)_2CHCH_3$	3.7	(LXXXII)	$CH_2CH_2CH_2OCH(C_2H_5)O$	2.8
(LIV)	$(C_5H_{11}O)_2CHCH_3$	4.0	(VII)	$CH_2CH_2CH_2CH_2OCH_2O$	1.9
(LV)	$(C_6H_{13}O)_2CHCH_3$	4.3	(LXXXIII)	$CH_2CH_2CH_2CH_2OCH(CH_3)O$	3.1
(LVI)	$(CH_3O)_2CH-C_3H_7$	3.8	(LXXXIV)	$CH_2CH_2CH_2CH_2OCH(C_2H_5)O$	3.6
(LVII)	$(C_2H_5O)_2CH-C_3H_7$	4.0	(LXXXV)	$CH_2CH_2CH_2CH_2OOH[CH(CH_3)_2]O$	3.0
(LVIII)	$(C_3H_7O)_2CH-C_3H_7$	4.2	(LXXXVI)	$CH_2CH_2OCH_2CH_2OCH_2O$	0.7
(LIX)	$(C_4H_9O)_2CH-C_3H_7$	4.4	(LXXXVII)	$CH_2C(CH_3)_2CH_2OCH(C_2H_5)O$	2.9
(LX)	$(C_6H_{11}O)_2CH-C_3H_7$	4.6	(LXXXVIII)	$CH_2OCH_2OCH_2CCH_2OCH_2OCH_2$	2.2
(XXVIII)	(iso-$C_3H_7O)_2CH_2$	1.6	(XC)	$CHO_2H_3CH_2OC(CH_3)_2O$	5.3
(LXI)	(iso-$C_4H_9O)_2CH_2$	2.0	(XCXXXXI)	$CH_2OCH(CH_3)OCH_2CCH_2OCH(CH_3)OCH_2$	1.4
(LXII)	(iso-$C_5H_{11}O)_2CH_2$	2.3	(XCI)	$CH_2CH_2CH(CH_3)OC(CH_3)(C_2H_5)$	1.2
(LXIII)	(iso-$C_3H_7O)_2CHCH_3$	2.9	(XCII)	$OCH_2CH_2CH_2CH_2CH-OCH_3$	1.4
(LXIV)	(iso-$C_4H_9O)_2CHCH_3$	3.2	(XCIII)	$OCH_2CH_2CH_2CH_2CHOC_3H_7$	1.8
(LXVI)	(iso-$C_3H_7O)_2CH-C_3H_7$	3.5	(XCIV)	$OCH_2CH_2CH_2CH_2CHOCHCH(CH_3)_2$	2.0
			(XCV)	$OCH_2CH_2CH_2CH_2CHOC_6H_{11}$	2.6
(LXVII)	(iso-$C_4H_9O)_2CH-C_3H_7$	3.8	(XCVI)	$OCH_2CH_2CH_2CH_2CHOC_4H_9$	1.9
(LXVIII)	(iso-$C_3H_7O)_2CH-CH(CH_3)_2$	2.9	(XCVII)	$C_6H_5CH_3$	0.2
(LXIX)	(iso-$C_4H_9O)_2CH-CH(CH_3)_2$	3.2	(XCVIII)	$CH_2CH_2OCH_2CH_2O$	0.8
(LXX)	(iso-$C_5H_{11}O)_2CH-OH(CH_3)_2$	3.5	(XCIX)	$OCH_2CH_2CH_2CH_2CHOC_8H_{17}$	3.2
(LXXI)	$(CH_3O)_2CH-CH(CH_3)_2$	2.9	(C)	$OCH_2CH_2CH_2CH_2CHO(C_8H_{17}$-s)	3.1
(LXXII)	$(C_2H_5O)_2CH-CH(CH_3)_2$	3.2	(CI)	$OCH_2CH_2CH_2CH_2CHO-C_4H_9$-t)	1.8
(LXXIII)	$(C_3H_7O)_2CH-CH(CH_3)_2$	3.5	(CII)	$[OCH_2CH_2CH_2CH_2CHO]_2(CH_2)_2$	4.6
(LXXIV)	$(C_4H_9O)CH-CH(CH_3)_2$	3.7	(CIII)	$OCH_2CH_2CH_2CHOC_5H_{11}$	3.0
(LXXV)	$(C_5H_{11}O)_2CH-CH(CH_3)_2$	4.0	(CIV)	$OCH_2CH_2CH_2CHOC_8H_{17}$	4.4
			(CV)	$OCH_2CH_2CH_2CHO-C_4H_9$-t)	2.9
			(CVI)	$OCH_2CH_2CH_2CHOC_6H_{11}$	5.2

The ratio of the rate constants for abstraction by an undecyl radical of a hydrogen atom from a substrate molecule and of a chlorine atom from tetrachloromethane

$$C_{11}\dot{H}_{23} + QH \xrightarrow{k_H} C_{11}H_{24} + Q^{\cdot}$$
$$C_{11}\dot{H}_{23} + CCl_4 \xrightarrow{k_{Cl}} C_{11}H_{23}Cl + CCl_3^{\cdot}$$

measures the reactivity of the acetal towards the radical (Table 4).[18,19] These results show that cyclic and linear acetals are more reactive than alkylbenzenes (XCVII), (CVII), (CVIII), and carboxylic acids (CX), (CXI) by factors of ten or more.

The ratio k_H/k_{Cl} increases with increase in length of the alkoxyl substituent in 1,1-dialkoxyalkanes and on attachment of an alkyl group to the carbon atom between the two oxygen atoms. The 1,1-dialkoxyethane (XXIX), (LII), (XXX), and (LIII) are about twice as active[18] as the corresponding formals (XXV)–(XXVII) and (XLIX). This indicates that a methyl group increases the activity of the bond between hydrogen and the tertiary carbon atom in acetals relative to the secondary methylenedioxy-links in formals. The 1,1-dialkoxyalkanes (LXIII) and (LXIV), which contain isoalkoxyl substituents, are somewhat less active than the acetals (XXX) and (LIII) with straight-chain alkoxy-groups. Table 5 gives relative rate constants for detachment of a hydrogen atom by undecyl radicals from carbon–hydrogen bonds of various strengths in 1,1-dialkoxyalkanes[18].

With change in size of the heterocyclic ring activity increases from 1,3-dioxacyclohexanes (CXV), (CXVI), (XXXII) through 1,3-dioxacycloheptanes (VII), (CXVII) to 1,3-dioxocyclopentanes (I), (CXIV).[19] These results agree well with data[24] on the influence of ring size on the activity of cyclic

acetals in free-radical isomerisation, in which the limiting stage of abstraction of the hydrogen atom from the 2-carbon atom in the substrate is effected by acyloxyalkyl radicals:

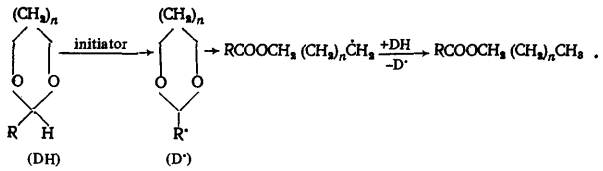
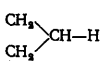
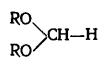
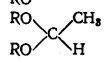


Table 4. Ratio of rate constants k_H/k_{Cl} for abstraction by undecyl radicals at 80 °C of a hydrogen atom from an acetal and of a chlorine atom from tetrachloromethane[18,19].

No.	Acetal (AH) formula	k_H/k_{Cl}	No.	Acetal (AH) formula	k_H/k_{Cl}
(XXV)	$(CH_3O)_2CH_2$	0.14	(XCVII)	$C_6H_5CH_3$	0.01*
(XXVI)	$(C_2H_5O)_2CH_2$	0.17	(CVII)	$C_6H_5CH_2CH_3$	0.02
(XXVII)	$(C_3H_7O)_2CH_2$	0.20	(CVIII)	$C_6H_5CH(CH_3)_2$	0.03
(XLIX)	$(C_4H_9O)_2CH_2$	0.24	(CIX)	CH_3COOH	0.02
(XXVIII)	$[(CH_3)_2CHO]_2CH_2$	0.16	(CX)	CH_3CH_2COOH	0.02
(LXI)	$[(CH_3)_2CHCH_2O]_2CH_2$	0.18	(CXI)	$CH_3CH_2CH_2COOH$	0.02
(LXII)	$[(CH_3)_2CHCH_2CH_2O]_2CH_2$	0.22	(CXII)	$C_4H_9OCH_3$	0.11
(LI)	$(C_5H_{11}O)_2CH_2$	0.57	(CXIII)	$(C_4H_9)_2O$	0.15
(XXIX)	$(CH_3O)_2CHCH_3$	0.31	(I)	$OCH_2CH_2OCH_2$	0.70
(LII)	$(C_2H_5O)_2CHCH_3$	0.37	(CXIV)	$OCH_2CH_2OCHC_3H_7$	0.98
(XXX)	$(C_3H_7O)_2CHCH_3$	0.40	(CXV)	$CH_2C(CH_3)_2CH_2OCH_2O$	0.22
(LIII)	$(C_4H_9O)_2CHCH_3$	0.44	(CXVI)	$CH_2C(CH_3)_2CH_2OCH(C_3H_7)O$	0.35
(LIV)	$(C_5H_{11}O)_2CHCH_3$	0.48	(XXXII)	$CH_2CH_2CH_2OCH(C_3H_7)O$	0.36
(LXIII)	$[(CH_3)_2CHO]_2CHCH_3$	0.32	(VII)	$CH_2CH_2CH_2CH_2OCH_2O$	0.35
(LXIV)	$[(CH_3)_2CHCH_2O]_2CHCH_3$	0.35	(CXVII)	$CH_2CH_2CH_2CH_2OCH(C_3H_7)O$	0.54

*From Ref. 23.

Table 5. Relative partial rate constants for abstraction by undecyl radicals at 80 °C of a hydrogen atom from C–H bonds in 1,1-dialkoxyalkanes[18].

Bond type	$10^2k_H/k_{Cl}$	Bond type	$10^2k_H/k_{Cl}$
	1.0		3.0
	1.2		25.0
	1.7		

Such a relationship indicates that the transition state is close to the final products[25]. The change in sp^3-hybridisation of the cyclic 2-carbon atom to sp^2, which occurs during detachment of the hydrogen atom, is least advantageous with the six-membered ring, which causes a decrease in the ratio k_H/k_{Cl}. The increase in activity of the 1,3-dioxacyclanes (CXIV), (CXVI), and (CXVII) with introduction of a 2-alkyl substituent into the ring is common to five-, six-, and seven-membered acetals. This effect is less marked with 1,3-dioxacyclopentanes (I) and (CXIV) than with 1,3-dioxacyclohexanes (CXV), (CXVI), and (XXXII) and 1,3-dioxacycloheptanes (VII) and (CXVII). This is attributed[19] to greater divergence of the bonds of the tervalent carbon atom from the planar structure in the resulting 2-alkyl-1,3-dioxacyclopent-2-yl radicals than in 2-alkyl-1,3-dioxacyclohex-2-yl and 2-alkyl-1,3-dioxacycloheptyl-2-yl radicals[2,8,11] and to the stabilising effect on them of the alkyl substituent.

The activities of linear and cyclic acetals towards phenyl radicals (Table 6) have been studied[20,21] by a method of competing reactions

$$C_6H_5^{\cdot} + DH \xrightarrow{k_H} C_6H_6 + D^{\cdot}$$

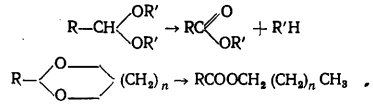
$$C_6H_5^{\cdot} + CCl_4 \xrightarrow{k_{Cl}} C_6H_5Cl + \dot{C}Cl_3$$

where DH is an acetal molecule. The qualitative pattern of relative reactivities and also the relations with the structure of the reactants and the nature of the substituents are on the whole the same as those for the reactions of acetals with undecyl radicals.

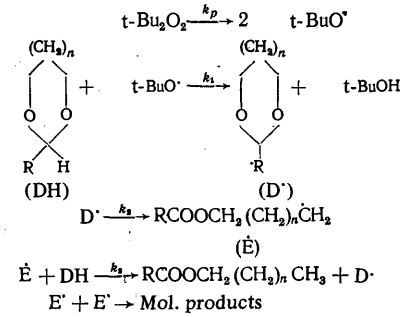
Relative partial rate constants for abstraction of a hydrogen atom from carbon–hydrogen bonds of different strengths in 1,1-dialkoxyalkanes and in 1,3-dioxacyclanes have been determined (Table 7).[20,21] The difference in activation energy for abstraction by a phenyl radical of a hydrogen atom from a 1,3-dioxacyclane and a chlorine atom from tetrachloromethane is 3.4–4.0 kcal mole^{-1}.[21]

IV. KINETICS AND MECHANISM OF HOMOLYTIC LIQUID-PHASE REACTIONS OF ACETALS

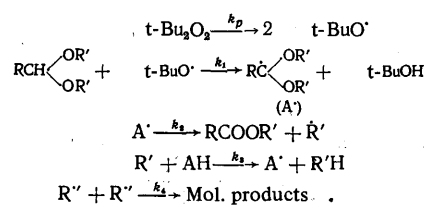
Formation of esters in the presence of radical initiators is a general reaction of linear and cyclic acetals[1,22–27]:



The reason is the greater activity in radical reactions of a carbon–hydrogen bond of a methine or methylene group located between two oxygen atoms. Kinetic study[28,29] of formation of the products has established a mechanism of isomerisation involving the sequence of primary steps—(*a*) in the case of 1,3-dioxacycloalkanes (DH)



or (*b*) in the case of 1,1-dialkoxyalkanes (AH)

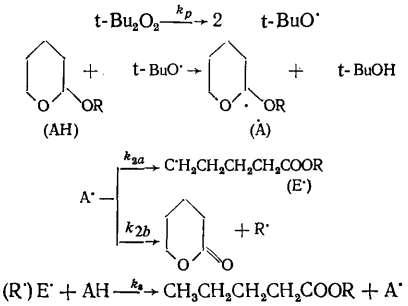


The difference in behaviour between cyclic and linear acetals is that a dialkoxycycloalkyl radical rearranges into a linear

Table 6. Ratio of rate constants k_H/k_{Cl} for abstraction by phenyl radicals of a hydrogen atom from an acetal and of a chlorine atom from tetrachloromethane[20,21].

No.	Acetal (AH) formula	$(k_H/k_{Cl})^{80°}$	No.	Acetal (AH) formula	$(k_H/k_{Cl})^{100°}$	$(k_H/k_{Cl})^{80°}$
(XXV)	$(CH_3O)_2CH_2$	2.9	(I)	$CH_2CH_2OCH_2O$	11.4	8.5
(XXVI)	$(C_2H_5O)_2CH_2$	3.1	(LXXVI)	$CH_2CH_2OCH(CH_3)O$	17.8	13.2
(XXVII)	$(C_3H_7O)_2CH_2$	3.5	(CXIV)	$CH_2CH_2OCH(C_3H_7)O$	—	13.8
(XLIX)	$(C_4H_9O)_2CH_2$	3.9	(CXIX)	$CH_2CH_2OCH(C_4H_9)O$	—	14.4
(XXVIII)	$[(CH_3)_2CHO]_2CH_2$	3.0	(CXX)	$CH_2CH_2OCH(C_6H_{13})O$	19.9	14.4
(LXI)	$[(CH_3)_2CHCH_2O]_2CH_2$	3.4	(LXXVII)	$CH_2CH_2OCH[CH(CH_3)_2]O$	—	12.8
(LXII)	$[(CH_3)_2CH(CH_2)_2CH_2O]_2CH_2$	3.8	(CXXI)	$CH_2CH_2OCH[CH_2CH(CH_3)_2]O$	—	13.1
(LI)	$(C_6H_{11}O)_2CH_2$	4.7	(CXV)	$CH_2C(CH_3)_2CH_2OCH_2O$	4.8	3.6
(XXIX)	$(CH_3O)_2CHCH_3$	4.4	(CXXII)	$CH_2C(CH_3)_2CH_2OCH(CH_3)O$	7.9	5.9
(LII)	$(C_2H_5O)_2CHCH_3$	4.8	(CXVI)	$CH_2C(CH_3)_2CH_2OCH(C_3H_7)O$	—	6.4
(XXX)	$(C_3H_7O)_2CHCH_3$	5.2	(CXXIII)	$CH_2C(CH_3)_2CH_2OCH(C_4H_9)O$	—	6.6
(LIII)	$(C_4H_9O)_2CHCH_3$	5.6	(CXXIV)	$CH_2C(CH_3)_2CH_2OCH(C_6H_{13})O$	—	7.0
(LIV)	$(C_6H_{11}O)_2CHCH_3$	6.6	(CXXV)	$CH_2C(CH_3)_2CH_2OCH[CH(CH_3)_2]O$	—	5.6
(LXIII)	$[(CH_3)_2CHO]_2CHCH_3$	4.8	(CXXVI)	$CH_2C(CH_3)_2CH_2OCH[CH_2CH(CH_3)_2]O$	—	5.9
(LXIV)	$[(CH_3)_2CHCH_2O]_2CHCH_3$	5.2	(LXXX)	$CH_2CH_2CH_2OCH(C_3H_7)O$	—	6.8
(XCVII)	$C_6H_5CH_3$	0.3	(VII)	$CH_2CH_2CH_2CH_2OCH_2O$	6.5	4.8
(CVII)	$C_6H_5CH_2CH_3$	1.1	(CXVII)	$CH_2CH_2CH_2CH_2OCH(C_3H_7)O$	—	9.5
(CVIII)	$C_6H_5CH(CH_3)_2$	1.4	(CXXVII)	$CH_2CH_2C(CH_3)_2OCH_2O$	—	3.2
(CXVIII)	$(C_3H_7)_2O$	1.2	(XXX)	$CH_2CH_2CH_2OCH_2O$	—	4.0
			(CXXVIII)	$CH_2CH_2CH_2CH_2CH_2CH_2$	—	2.7

acyloxyalkyl radical, whereas an αα-dialkoxyalkyl radical fragments with formation of an ester and an alkyl radical. These two routes are followed simultaneously in the isomerisation of cyclolinear acetals of 2-alkoxyoxans[30-32], when the 2-alkoxyoxacyclohex-2-yl radical formed is converted into an alkyl valerate or δ-valerolactone by rupture of an endocyclic or exocyclic carbon–oxygen bond:



$$(R')E^{\cdot} + AH \xrightarrow{k_3} CH_3CH_2CH_2CH_2COOR + A^{\cdot}$$

$$(R')E^{\cdot} + E^{\cdot}(R') \xrightarrow{k_4} \text{Mol. products}.$$

The variation in activity of the cyclic compounds (Table 8) depends on the size of the ring. Three competing factors—degree of hybridisation, strain in the ring, and polar effects—were taken into account[33] in considering the reactivity of these compounds with respect to isomerisation. The reactivities of the formals (I), (LXXX), (VII), (CXXIX), (XXXVI), and (CXXX) correlate with the rates of formation of carbonium ions and of decomposition of azo-compounds[33], which in view of conclusions in Ref. 34 indicates almost complete rupture of the bond in the rate-determining step. Hence the transition state must be closer in structure to the products than to the initial species. The 2-carbon atom (the reaction centre) passes from sp^3- to sp^2-hybridisation, which weakens the effect of steric hindrance in the case of 1,3-dioxolan (I), but in the reaction with seven-, eight-, and nine-membered structures (VII), (CXXIX), and (CXXX) weakens transannular interaction. When 1,3,6-trioxacyclooctane (XXXVI), in which repulsion between atoms at positions 2 and 6 is not possible, acceleration of the reaction is not observed. In the cyclohexane analogue (LXXX) the reaction is slowed down, since the almost ideal tetrahedral configuration is disrupted on passing to sp^2-hybridisation.

Table 7. Relative partial rate constants for abstraction by phenyl radicals of a hydrogen atom from carbon–hydrogen bonds in 1,1-dialkoxyalkanes at 100 °C and 1,3-dioxacyclanes at 80 °C.[20,21]

Bond in dialkoxyalkane	$(k_H/k_{Cl})^{100°}$	Bond in dioxacyclane	$(k_H/k_{Cl})^{80°}$
	0.1		
$ROCH_2-H$	0.1		0.25
$ROCH(CH_3)-H$	0.2		0.40
$(RO)_2CH-H$	1.2		0.95
$(RO)_2C(CH_3)-H$	4.0		4.2

*In a ring.

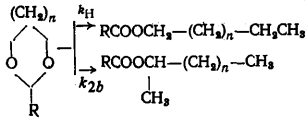
Differences in activity between the cyclic acetals (LXXVI)–(LXXIX), (LXXXI), (LXXXIII), (LXXXV), and (CXXI) are determined[17,23] by the capacity of the $C_{(2)}$–H bond for homolysis on reaction with primary alkyl radicals (Table 8). All derivatives of aliphatic aldehydes isomerise at rates exceeding the rate of isomerisation of the corresponding formals by factors of 2–3 (allowing for the number of active hydrogen atoms). The introduction of a 2-methyl group causes almost identical increases in the activity of five-, six-, and seven-membered cyclic acetals in the abstraction of a hydrogen atom by t-butoxyl,[17] undecyl,[19] and alkyl [17,23] radicals; this can be attributed to enhancement of the energy of the ground state, which is consistent with data[33] showing that increase in such energy facilitates homolysis of the bonds being broken. The slight increase in reactivity of the benzaldehyde derivative (LXXIX) is explained[35] by the non-planar structure of the 2-phenyl-1,3-dioxacycloalk-2-yl radical.

Table 8. Kinetic parameters for the isomerisation of cyclic acetals [0.3 M $(t\text{-}C_4H_9)_2O_2$].[17,23,36]

No.	Acetal formula	$10^3 \cdot k_s/k_4^{1/2}$, $M^{-1/2}\,s^{-1/2}$			
		120°	130°	140°	150°
(I)	$OCH_2CH_2OCH_2$	4.3	5.9	10.2	15.8
(LXXX)	$OCH_2CH_2CH_2OCH_2$	0.66	1.0	1.49	2.16
(VII)	$OCH_2CH_2CH_2CH_2OCH_2$	1.32	2.5	2.74	3.95
(CXXIX)	$OCH_2(CH_2)_3CH_2OCH_2$	—	5.6	—	—
(XXXVI)	$OCH_2CH_2OCH_2CH_2OCH_2$	—	1.1	—	—
(CXXX)	$OCH_2(CH_2)_4CH_2OCH_2$	—	8.0	—	—
(LXXVI)	$OCH_2CH_2OCHCH_3$	8.03	7.0	8.15	9.56
(LXXXI)	$OCH_2CH_2CH_2OCHCH_3$	1.26	1.84	2.72	5.14
(LXXXIII)	$OCH_2(CH_2)_2CH_2OCHCH_3$	2.19	3.16	4.57	6.60
(CXXI)	$OCH_2CH_2OCHCH_2CH(CH_3)_2$	5.01	7.12	10.0	14.1
(LXXIX)	$OCH_2CH_2OCHC_6H_5$	6.26	8.06	10.4	13.7
(CXXXI)	$OCH(CH_3)CH(CH_3)OCH_2$	3.1	4.0	6.4	9.0
(CXXXII)	$OCH(CH_3)CH_2CH(CH_3)OCH_2$	0.26	0.4	0.6	0.9
(CXXXIII)	$OCH(CH_3)CH_2CH_2CH(CH_3)OCH_2$	0.88	1.4	2.17	3.36

The lower reactivity of the cyclic acetals (CXXXI)–(CXXXIII) of di-secondary glycols (Table 8) than of their unsubstituted analogues is due not to change in strength of the $C_{(2)}$–H bond undergoing rupture but to differences in activity between the radicals carrying the chain[36].

2,4-Disubstituted 1,3-dioxacyclanes (Table 9) during isomerisation form esters of primary and secondary alcohols[17,37]:



Preferential formation of straight-chain esters is due[11,13,17,37] to the greater rate of formation of a secondary than of a primary radical on ring opening in a cyclic radical. Isomerisation of the 1,3-dioxans (CXXXIV), (CXXXV), and (CXXXVIII) into straight-chain esters is more selective than that of the 1,3-dioxolans (CXXXVI) and (CXXXVII) probably because the transition state is closer to the final products in the rearrangement of a six-membered than of a five-membered ring[17,37].

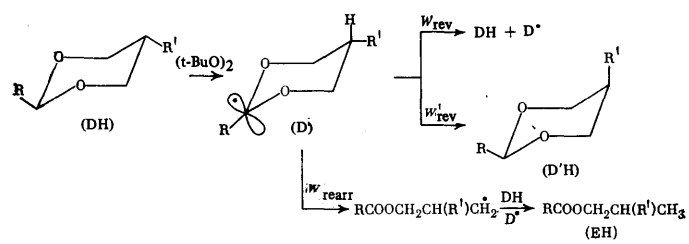
The only product of isomerisation of 4,4-dimethyl-1,3-dioxan—a formal of a primary–tertiary glycol—under the influence of t-butyl peroxide is isopentyl formate[17]. This indicates that the rate constant of rearrangement of a cyclic dialkoxyalkyl radical into a tertiary formyloxyalkyl radical exceeds the rate constant of rearrangement into a primary radical by factors of ten or more[13].

Table 9. Isomerisation of 2,4-disubstituted 1,3-dioxacyclanes[17,37].

No.	Acetal formula	k_H/k_i			ΔE^*, kcal mole^{-1}
		120°	130°	150°	
(CXXXIV)	$OCH(CH_3)CH_2CH_2OCHCH(CH_3)_2$	3.8	3.6	3.2	2.2
(CXXXV)	$OCH(CH_3)CH_2CH_2OCH_2$	6.0	5.6	4.9	2.4
(CXXXVI)	$OCH(CH_3)CH_2OCHCH_3$	1.9	1.8	1.7	1.3
(CXXXVII)	$OCH(CH_3)CH_2OCHCH(CH_3)_2$	1.8	1.7	1.6	1.2
(CXXXVIII)	$OCH(CH_3)CH_2CH_2OCHC_6H_5$	—	5.0**	—	—

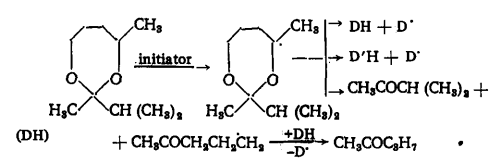
*From Ref.40, at 135 °C.
**$\Delta E = E_H - E_i$.

In the reaction initiated by t-butyl peroxide individual stereoisomers of 2,5-dialkyl-1,3-dioxacyclohexanes not only form the corresponding esters but also undergo configurational isomerisation[11,38]:



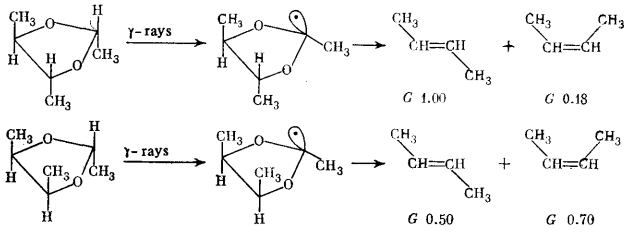
The reverse transition—from stereoisomers having an equatorial–axial arrangement of groups to isomers with a diequatorial arrangement of alkyl substituents—is also possible (DH′ → DH). It is noteworthy that at 135 °C the rate of rearrangement of 2,5-dialkyl-1,3-dioxacyclohex-2-yl radicals w_{rearr} exceeds the rate of epimerisation w'_{rev} by factors of 4–7.

Radical epimerisation of 1,3-dioxacyclanes can involve alkoxycycloalkyl radicals. Thus reaction between the low-boiling stereoisomer of 2-isopropyl-2,4-dimethyl-1,3-dioxacycloheptane (DH) and t-butyl perbenzoate at 100 °C yields methyl propyl and isopropyl methyl ketones together with the high-boiling isomer (D′H):[39]



Comparison of results in Refs. 11, 38, and 39 indicates that the ring breaks down more rapidly when dialkoxyalkyl radicals are involved. This is because rearrangement of a cyclic dialkoxyalkyl radical with formation of a carboxy-group is energetically more advantageous than is rearrangement of a cyclic monoalkoxyalkyl radical with formation of a carbonyl group[39].

1,3-Dioxacyclopent-2-yl radicals generated in aqueous medium by γ-irradiation may break down by a concerted mechanism with simultaneous rupture of two bonds[40]. Thus radiolysis of *trans*- and *cis*-2,4,5-trimethyl-1,3-dioxolans forms both *cis*- and *trans*-but-2-enes:



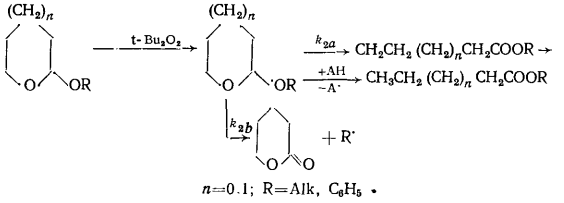
where *G* is the quantum yield. The initial *trans*-isomer gives predominantly *trans*-but-2-ene, and the *cis*-isomer gives mainly *cis*-but-2-ene.

Table 10. Kinetic parameters for homolytic reactions of 2-alkoxyoxacyclanes at 130 °C.[30]

No.	Acetal formula	k_{2b}/k_2*	k_{2a}/k_2	k_{2a}/k_{2b}	$10^3 k_2/k_4^{1/2}$, $M^{-1/2} s^{-1/2}$
(XCII)	$O(CH_2)_4CHOCH_3$	—	1.0	10.0	1.8
(XCIV)	$O(CH_2)_4CHOCH(CH_3)_2$	0.72	0.28	0.4	0.7
(CI)	$O(CH_2)_4CHOC(CH_3)_3$	1.0	—	0.4	0.2
(XCV)	$O(CH_2)_4CHO-C_6H_{11}$	0.55	0.45	0.8	1.1
(CVI)	$O(CH_2)_5CHOC_6H_{11}$	0.70	0.30	0.4	1.9

*$k_2 = k_{2a} + k_{2b}$.

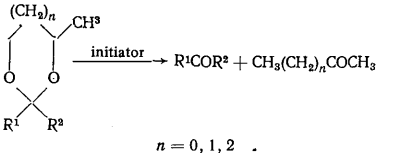
The type of reaction and the relative activity of 2-alkoxyoxacycloalkanes (Table 10) depend on the structure of the alkoxy-substituent and on the size of the ring[30-32]. 2-Alkoxyoxolans (CVI) are more active than the corresponding oxans (XCV):[30]



n=0,1; R=Alk, C_6H_5.

Derivatives of primary alcohols—especially of methanol (XCII)—give predominantly the isomeric linear esters, whereas derivatives of tertiary alcohols mainly fragment with formation of δ-valerolactone[30,32]. Under otherwise similar conditions the ratio of ester to lactone is higher in the case of oxans (XCV) than with their five-membered analogues (CVI),[30] since the rate of rearrangement of cyclic dialkoxyalkyl radicals increases with ring size[11,13,41]. 2-Methoxyoxan (XCII) and 2-methyl-1,3-dioxan (LXXXI) are closely similar in reactivity. The factor determining the reactivity of cyclic acetals, independently of their structure, is obviously the presence of two oxygen atoms located α to the ruptured carbon–hydrogen bond[1].

2,2-Dialkyl-4-methyl-1,3-dioxacyclanes—cyclic ketals of primary–secondary glycols—are converted into carbonyl compounds under the influence of radical initiators, with ring cleavage at the two carbon–oxygen bonds[17,42]:



$n = 0, 1, 2$.

Here the reaction centre is a methine group adjacent to one oxygen atom. The reactivity of ketals, like that of acetals, is determined by the size of the ring, the presence of substituents promoting homolysis of the $C_{(4)}$–H bond, and the activity of the radicals carrying the chain.

Table 11. Kinetic parameters for the liquid-phase free-radical conversion of 1,1-dialkoxyalkanes $R^1CH(OR^2)_2$ into esters R^1COOR^2.[24-26]

Acetal No.	R^1	R^2	$10^3 k_2/k_4^{1/2}$, $M^{-1/2} s^{-1/2}$	$\lg A_2^*/A_4^{1/2}$	$E_2 - 0.5E_4$, kcal mole^{-1}
(XXVI)	H	C_2H_5	0.31	0.61	7.6±0.5
(XXVII)	H	C_3H_7	0.32	4.40	14.6±0.3
(XXVIII)	H	iso-C_3H_7	0.34	6.90	19.2±0.8
(XLIX)	H	C_4H_9	0.50	5.90	16.9±0.5
(LXI)	H	iso-C_4H_9	0.45	6.90	18.8±0.3
(L)	H	C_5H_{11}	1.19	3.40	11.7±0.3
(LXII)	H	iso-C_5H_{11}	1.01	3.90	12.8±0.3
(LI)	H	cyclo-C_6H_{11}	0.83	0.44	6.5±0.3
(XXIX)	CH_3	CH_3	1.49	3.84	12.3±0.3
(LII)	CH_3	C_2H_5	0.86	1.54	8.5±0.2
(XXX)	CH_3	C_3H_7	1.17	1.30	7.8±0.3
(LIII)	CH_3	C_4H_9	2.30	1.48	7.6±0.3
(LXIV)	CH_3	iso-C_4H_9	0.23	2.63	11.4±0.2
(CXXXIX)	CH_3	s-C_4H_9	1.41	0.73	6.6±0.3
(LIV)	CH_3	C_5H_{11}	1.96	1.08	7.0±0.8
(CXL)	CH_3	iso-C_5H_{11}	1.67	2.80	10.3±0.5
(CXLI)	CH_3	C_6H_{13}	1.23	1.64	8.4±0.5
(CXLII)	C_6H_5	C_2H_5	1.38	3.10	11.5±0.5

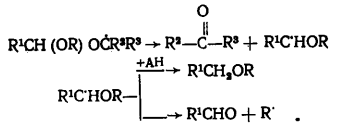
*Pre-exponential factor.

Kinetic study of the homolytic reactions of 1,1-dialkoxyalkanes[22-27] has established that their activity increases in the sequence diethoxymethane < 1,1-diethoxyethane < phenyldiethoxymethane (Table 11). Hence groups capable of delocalising the unpaired electron and thereby stabilising the intermediate dialkoxyalkyl radical enhance the reactivity of acetals.

The activity of 1,1-dialkoxyalkanes in homolytic liquid-phase reactions depends little on the size of the alkoxy-group[25].

The lower activity of 1,1-dialkoxyalkanes than of 1,3-dioxacyclanes is attributed to greater stability of carbon–hydrogen bonds in linear than in cyclic acetals, and also to the greater advantage for cyclic systems of change to an sp^2-state of the sp^3-hybridised carbon atom between the two oxygen atoms[24,25].

Formation of carbonyl compounds and ethers in the course of homolytic liquid-phase reactions is characteristic of derivatives of higher aliphatic alcohols[25]. Their rates of accumulation are lower than that of the formation of esters by factors of 2–3 and 8–10 respectively. Ethers and carbonyl compounds are formed as a result of one- and two-stage fragmentations of monoalkoxyalkyl radicals:



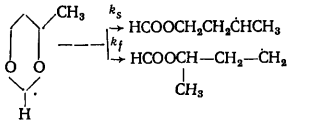
The selectivity of formation of esters diminishes on passing from derivatives of primary to those of secondary alcohols[24–26], owing to the decrease in the difference in reactivity of carbon–hydrogen bonds adjacent to one or two oxygen atoms. The difference in activation energy of rupture of such bonds by alkyl radicals is 1.0–2.5 kcal mole^{-1}.[24–26]

The rate of accumulation of ethers R'CH$_2$OR is lower than that of formation of carbonyl compounds R'CHO by factors of 3–6. This indicates that the rate of unimolecular breakdown of monoalkoxyalkyl radicals exceeds the rate of abstraction of a hydrogen atom from a substrate molecule[24].

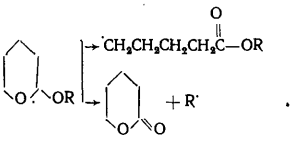
Formation of esters is also observed when reactions of 1,1-dialkoxyalkanes (XLIX) and (CXLI) are initiated by the photochemical decomposition of t-butyl peroxide (at 20 °C), but their rate of accumulation is far lower than the rate of initiation, and over a wide range is independent of the substrate concentration[43]. Under these conditions chain termination takes place mainly on dialkoxyalkyl radicals, fragmentation of which is the rate-determining stage. The rate constant of rearrangement (at 20 °C) of dialkoxyalkyl radicals ·C(OR)$_2$CH$_3$ (R = n-C$_4$H$_9$, n-C$_6$H$_{13}$) including primary alkoxy-substituents is $k_2 \approx 10$ s^{-1}.[24,43]

The influence of high pressure on the kinetics and the mechanism of the homolytic conversion of acetals into esters has been studied[11,27,30,44–47]. In the isomerisation of 2-isopropyl-1,3-dioxolan (LXXVII) the kinetic parameter $k_3/k_4^{1/2}$ remains almost unchanged with increase in pressure[11,44]. The reason is that abstraction of a hydrogen atom by primary alkyl radicals is only slightly accelerated with increase in pressure (this effect is more typical of secondary and tertiary radicals[48]), while recombination, governed by the rate of interaction of radicals in the cage, may be enhanced[44].

In the isomerisation of 4-methyl-1,3-dioxan (CXXXV) the chain is carried mainly by secondary alkyl radicals, and increasing the pressure to 7500 atm increases $k_3/k_4^{1/2}$ by factors of 2.0–2.5.[11,45] The selectivity of formation of a straight-chain ester in the isomerisation of 4-methyl-1,3-dioxolan increases with pressure, for the transition state is closer to the initial state along the reaction coordinate for the formation of a secondary than of a primary alkyl radical:

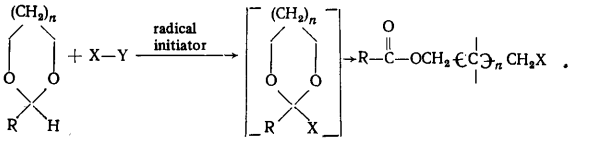


The stage of rearrangement of the 4-methyl-1,3-dioxacyclohex-2-yl radical differs little in volume of activation depending on whether a primary or a secondary acyloxyalkyl radical is formed: $\Delta V_{sf}^{\neq} \approx 3$ cm^3 mole^{-1}.[45] The direction of homolytic transformation of 2-alkoxyoxans is more noticeably influenced by pressure[30,46,47], rise in which increases the proportion of δ-valerolactone relative to the ester. The explanation is that rearrangement in both directions is slowed down[30,46], but the ring-opening rate constant is more strongly lowered:



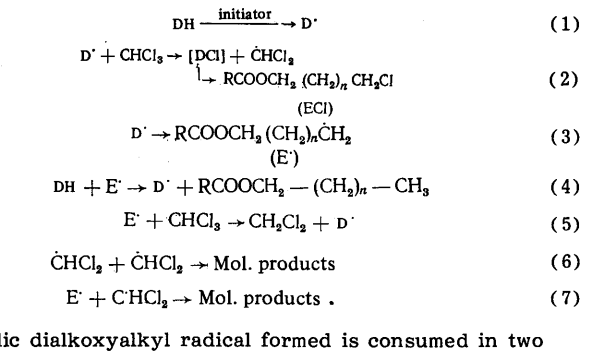
In conversion of the 1,1-dialkoxyalkanes (LXI) and (LXIV) into esters[27] the ratio of the rates of formation of isobutyl acetate and formate increases with pressure, as a consequence of the difference in reactivity towards homolytic cleavage between the secondary and tertiary carbon–hydrogen bonds in (LXI) and (LXIV). This agrees well with data showing that rise in pressure accelerates more strongly the reaction that takes place more rapidly under normal conditions[49,50].

There is much published information[1,38,51–56] indicating that 1,3-dioxacyclanes are converted under the influence of radical initiators in the presence of halogenating agents X–Y (chlorine, *N*-bromosuccinimide, polyhalogenoalkanes) into the corresponding halogenated carboxylic esters:



Formation of the latter involves[1,51–53] an intermediate unstable[53] cyclic dialkoxyalkyl halide, which rapidly isomerises into the corresponding halogenated ester. Isomerisation of the halide entails intramolecular nucleophilic substitution as a result of attack by an X$^-$ anion at a carbon atom attached to an oxygen atom. The photolysis of optically active 2-methyl-4-phenyl-1,3-dioxolan in the presence of trichlorofluoromethane, sensitised by benzophenone, yields α-chlorophenethyl acetate with complete inversion of configuration[5].

When 1,3-dioxacyclanes undergo homolytic isomerisation in halogenoalkanes (tetrachloromethane, chloroform, bromotrichloromethane, etc.), formation of esters is accompanied by that of halogenated carboxylates[38,54–57], the latter by chain transfer to the halogenoalkane[54]. Kinetic study of the accumulation of chloroesters in chloroform suggested[38,55–57] for their formation the mechanism



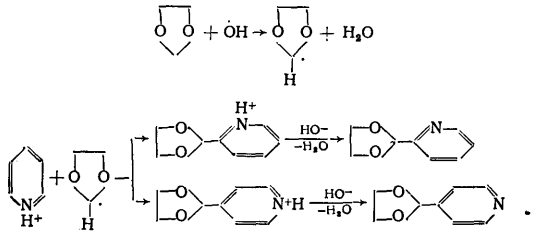
The cyclic dialkoxyalkyl radical formed is consumed in two ways: bimolecular abstraction of a chlorine atom from chloroform gives an unstable[53] 2-chloro-1,3-dioxacyclane DCl, which under the reaction conditions undergoes unimolecular conversion into the chloroester; and unimolecular rearrangement (3) into linear acyloxyalkyl radicals, which then abstract a chlorine atom from chloroform (5), finally gives the chloroester. The relative contributions of reactions (2) and (5) to

the kinetics of accumulation of the chloroester depend on the temperature[38]: at 130 °C (with t-butyl peroxide as initiator) the chloroester accumulates by both reactions, whereas at 80 °C (initiator benzoyl peroxide) reaction (2) is the chief pathway for the formation of ECl; unchlorinated esters are not found[38].

The rate-determining stage is rupture of a carbon–hydrogen bond by a dichloromethyl radical[38]. Termination takes place on such radicals. The reactivity of 1,3-dioxacyclanes towards conversion into chlorinated esters has been studied[38, 55–57]. Values of the kinetic parameter $k_3/k_4^{1/2}$, which characterise the activity of acetals towards the dichloromethyl radical at 80 °C, show[38] that it is comparable with their reactivity towards alkyl radicals only at 120–130 °C. The reason given[38] for the enhanced reactivity of dichloromethyl radicals is that a carbon–hydrogen bond is stronger in dichloromethane than in the methyl group of a normal hydrocarbon by 1.5–2.0 kcal mole^{-1}. [58,59] The nature of the substituent has little effect on the strength of the ruptured $C_{(2)}$–H bond.

Results fully consistent with these conclusions have been obtained for the conversion of 1,3-dioxacyclanes into chloroesters in the presence of 1,1,1-trichloroethane. Dichloromethyl and 1,1-dichloroethyl radicals show the same tendency to abstract a hydrogen atom. The presence of two halogenating agents[60] (e.g. tetrachloromethane with *N*-bromosuccinimide or with bromotrichloromethane) leads to parallel formation of bromo- and chloro-esters. Preferential formation of the former is attributed[60] to greater stability of the carbon–chlorine bond.

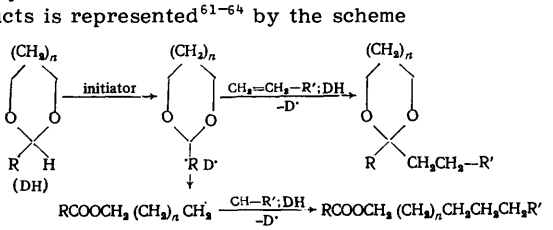
A hydrogen atom located between two oxygen atoms in 1,3-dioxolan can be replaced by a pyridine residue[61]. Thus reaction between protonated pyridine and 1,3-dioxolan in the presence of iron(II) sulphate together with hydrogen peroxide to supply hydroxyl radicals gives 2- and 4-(1,3-dioxacyclopent-2-yl)pyridines:



The 2-isomer is formed preferentially, which is on the whole characteristic of homolytic substitution of protonated heteroaromatic bases under the influence of nucleophilic carbon-centred radicals.

V. RADICAL ADDITION OF ACETALS TO ALK-1-ENES

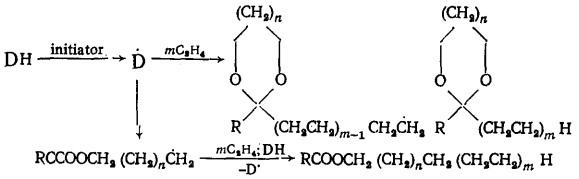
Addition of 1,3-dioxacyclanes to terminal alkenes (hexene, octene, ethylene) yields the corresponding 2-alkylated 1,3-dioxacyclanes and esters[62–70]. The formation of addition products is represented[61–64] by the scheme



$n = 0, 1, 2$; R′ = H, C_4H_9, or C_6H_{13}; R = H, or Alk.

The relative proportions of linear and cyclic products depend[41,61] on the temperature and the structure of the dioxacyclane. Below 50 °C the main products are 2-alkyl-1,3-dioxacyclanes. With rise in temperature the yield of esters increases. Increase in ring size has a similar effect, which is explained[61] by increase in the rate of unimolecular rearrangement of dialkoxyalkyl radicals on passing from five- to seven-membered rings[11,13]. The yield of cyclic products increases on passing from formals to acetals, owing[61,62] to the lower rate of unimolecular rearrangement of tertiary than of secondary dialkoxycycloalkyl radicals[11,13,41]. Substituents capable of delocalising the unpaired electron at position 2 in the 1,3-dioxacyclane somewhat increase the yield of 2-alkyl-1,3-dioxacyclane[61].

Two series of products—ester telomer-homologues and 2-alkyl-1,3-dioxacyclanes—have been identified[65–70] in the radical telomerisation of ethylene by cyclic acetals at 50° to 150 °C. The mechanism



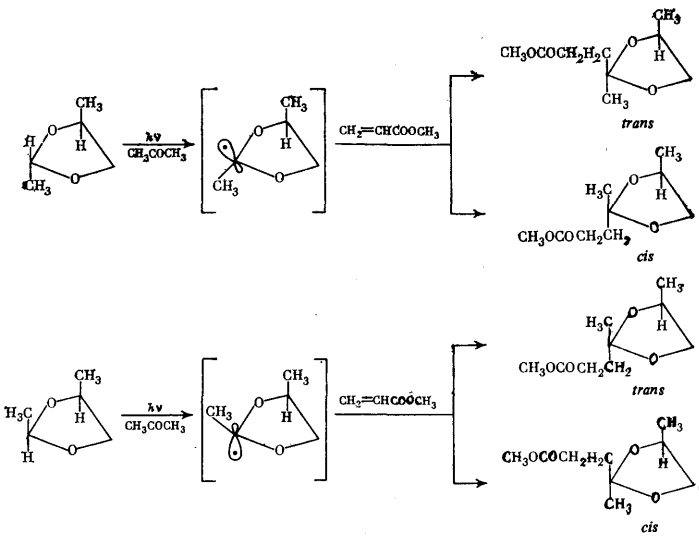
was suggested[65–70] for the formation of these products. The cyclic dialkoxyalkyl radical adds to ethylene or else gives a linear acyloxyalkyl radical by intramolecular rearrangement. The latter adds to ethylene to form esters. The values found[65–68] for the partial chain-transfer constants ($C_n \cong 0.1$ to 0.3) characterise 1,3-dioxacyclanes as telogens of medium activity. The fact that C_n is independent of the number T_n of monomer units already added to the growing radical indicates that the 1,3-dioxacyclane substituent exerts no polar effect.

Telomerisation of a five-membered cyclic formal, 1,3-dioxolan, is accompanied by formation of a new series of products, 2-alkyl-2-butyl-1,3-dioxolans[65,69], which is attributed[69] to rearrangement of the growing radical T_n ($n = 2$) with 1,5-migration of a hydrogen atom. Such transfer is made possible by an unstrained transition state having a six-membered ring structure[65,69].

The radical telomerisation of ethylene by 2,4-dimethyl-1,3-dioxan (VI) (in the presence of dicyclohexyl peroxodicarbonate at 50 °C) yields stereoisomeric 2-alkyl-2,4-dimethyl-1,3-dioxans[71]. Isomers having an axial—equatorial arrangement of methyl groups are formed preferentially. This is assumed[71] to be due to the shielding effect of the axial $H_{(1)}$–$H_{(6)}$ atoms or to the non-planar structure[11,14,23] of the 2,4-dimethyl-1,3-dioxacyclohex-2-yl radical (XX). The telomerisation of ethylene by 4-methyl-1,3-dioxolan (benzoyl peroxide at 80 °C) also yields predominantly *trans*-2-alkyl-4-methyl-1,3-dioxolans, which is attributed[72] to the same causes[71].

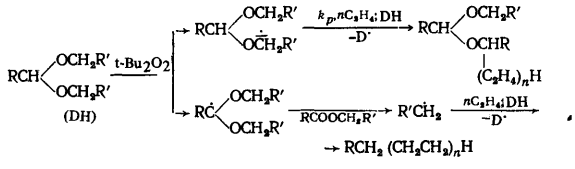
Photochemical addition of *cis*- or *trans*-2,4-dimethyl-1,3-dioxolan to methyl acrylate (at −78 °C) gives a mixture of geometric isomers, in which that with a *cis*- or *trans*-

arrangement of the methyl groups respectively predominates[73]:



Such stereoselective addition of methyl acrylate is attributed[73] to the pyramidal structure of the 2,4-dimethyl-1,3-dioxacyclopent-2-yl radical, which under the reaction conditions (−78 °C) partly retains the original structure. With rise in temperature above 20 °C the *cis*-dimethyl isomer is formed preferentially. Inversion of the pyramid of the tervalent carbon atom apparently occurs readily with rise in temperature, and the stereoselectivity of addition is determined by the presence of the 4-methyl group.

The radical telomerisation of ethylene by 1,1-dialkoxyalkanes[74–77] gives unsymmetrical linear acetals formed by the addition of monoalkoxyalkyl radicals to ethylene; esters and unsaturated hydrocarbons are also formed. The latter results from addition to ethylene of fragmentation products from the 1,1-dialkoxyalkanes. The telomerisation of ethylene by 1,1-dialkoxyalkanes initiated by t-butyl peroxide is represented[74–77] by the scheme

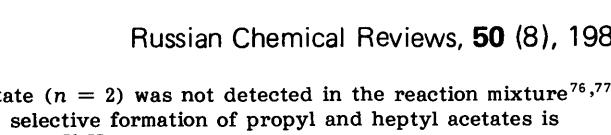


Products of the addition of dialkoxyalkyl radicals to ethylene are not detected, for linear radicals of this type are unstable[13]. Even at 20 °C they break down unimolecularly to form esters and alkyl radicals[9,23,76,77].

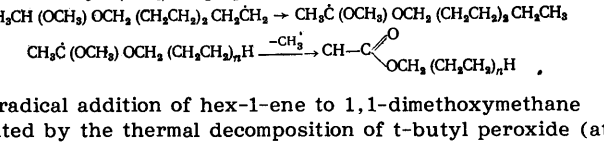
The radical telomerisation of ethylene by 1,1-dialkoxyalkanes is characterised[76,77] by partial chain-transfer constants $C_n = k_n/k_p$; for example, the values of these constants for diethoxymethane are[76]

$$C_1 = 0.18 \pm 0.02;\ C_2 = 0.19 \pm 0.02;\ C_3 = 0.19 \pm 0.02 \text{ (Ref.76)}.$$

Hence linear acetals are comparatively ineffective reaction-chain carriers and are telogens of moderate activity. Since C_n is independent of the number n of monomer units, the acetal radical exerts no polar effect on chain transfer[76]. In the telomerisation of ethylene by 1,1-dimethoxymethane not only unsymmetrical linear acetals but also propyl and heptyl acetates (n = 1, 3) have been identified, though pentyl acetate (n = 2) was not detected in the reaction mixture[76,77]. The selective formation of propyl and heptyl acetates is explained[76,77] by the novel process (for this reaction) of rearrangement of the first and third growing radicals (n = 1, 3) with 1,5- and 1,9-migration of a hydrogen atom:



The radical addition of hex-1-ene to 1,1-dimethoxymethane initiated by the thermal decomposition of t-butyl peroxide (at 150 °C) is also accompanied by rearrangement with 1,5-migration of a hydrogen atom[76,77]:



The ease with which such migration takes place is due to the unstrained character of the transition state, whose geometry is similar to that of the cyclohexane ring.

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On the whole the above features of homolytic liquid-phase reactions of cyclic and linear acetals and related compounds are due to the presence of carbon–hydrogen bonds activated by oxygen atoms. The selectivity of formation of dialkoxyalkyl radicals and their reactivity towards various reagents mainly determine the rate and direction of transformation of acetals in solution.

The information surveyed on the homolytic reactions of acetals in solution demonstrates the prospects for using such reactions to generate substituted carbon-centred radicals and employing them in organic synthesis.

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