Radiation Chemistry of Acetals. Part 4. Photolysis (λ 185) of Liquid 1,3-Dioxolan and 2,2-Dimethyl-1,3-dioxolan [1]

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The 185 nm photolysis of the title compounds has been carried out at different temperatures. The quantum yields of the products give satisfactory material balances. The major primary process appears to be ring cleavage at the C(1)–C(5) bond, the biradical $\cdot CH_2CH_2{-}O{-}CR_2{-}O\cdot$ being an intermediate. Other decomposition pathways may be molecular in nature. Major products from the photolysis at 20 °C of 2,2-dimethyldioxolan are acetone (ϕ = 0.27), propyl acetate (0.24), ethylene (0.18), acetaldehyde (0.13), methyl acetate (0.12), and ethylene oxide (0.11). Dioxolan-2-yl and dioxolan-4-yl radicals are also involved in the photodecomposition. The former radicals are found to rearrange to the β-acyloxyethyl radicals. In the unsubstituted 1,3-dioxolan, the β-formyloxyethyl radical acts as a chain carrier in a reaction leading to ethyl formate as the main product.

ALTHOUGH in the photolysis of open-chain acetals [1-3] initially a C–O bond is cleaved, as it is with aliphatic ethers,[4-7] the question arose as to whether ring compounds differ from their open-chain counterparts. In the gas-phase photolysis of 1,3-dioxolan,[8] large amounts of CO_2 are formed, a product which is completely absent in the liquid-phase photolysis of the open-chain acetals.[1-3]

In the present paper it will be shown that the behaviour of the liquid 1,3-dioxolans is strikingly different from that in the gas phase, probably because thermalization of the primary fragments is more efficient in the liquid.

EXPERIMENTAL

1,3-Dioxolan (B.A.S.F.) and 2,2-dimethyl-1,3-dioxolan (Fluka) were fractionated to a g.c. purity of >99.98%. Samples were dearated by purging with argon or helium, irradiated in a Suprasil QS cell with a low-pressure Hg arc, and (except for formic acid) analysed by g.c. and g.c.–m.s. using previously described methods.[5,9] When set aside, 1,3-dioxolan appears to deteriorate more easily than its dimethyl analogue. Samples of such 'stale' 1,3-dioxolan showed a red-shifted end absorption and gave hydrogen quantum yields much higher than that from fresh samples.

TABLE 1

Photolysis (λ 185) of 1,3-dioxolan. Product quantum yields at various temperatures

		8 °C	20 °C	35 °C	50 °C	65 °C
(1)	H_2	*a*	0.20	*a*	0.18	*a*
(2)	CO	*a*	0.014	*a*	*a*	*a*
(3)	CO_2	*a*	0.092	0.095	0.091	0.095
(4)	CH_4	*a*	0.8×10^{-3}	0.7×10^{-3}	0.9×10^{-3}	1.0×10^{-3}
(5)	C_2H_4	*a*	0.24	0.21	0.21	0.21
(6)	C_2H_6	*a*	0.9×10^{-3}	0.7×10^{-3}	0.9×10^{-3}	1.2×10^{-3}
(7)	CH_2O	*a*	*a*	*a*	*a*	*a*
(8)	HCO_2H	*a*	0.16	0.17	0.17	*a*
(9)	MeCHO	0.16	0.15	0.17	0.15	0.15
(10)	$\overline{CH_2CH_2O}$	0.18	0.18	0.17	0.15	0.16
(11)	$HCO_2CH{=}CH_2$	0.05	0.04	0.05	0.04	0.04
(12)	HCO_2Et	0.34	0.38	0.61	0.94	1.55
(13)	$[\overline{O\cdot(CH_2)_2\cdot O\cdot CH}\text{-}]_2$ } *b*	0.14	0.15	0.15	0.16	0.12
(14)	$[\overline{CH_2\cdot O\cdot CH_2\cdot O\cdot CH}\text{-}]_2$ } *b*					
(15)	*c*	0.02	0.02	0.03	0.03	0.06
(16)	$(CH_2)_4(OCHO)_2$ [d]	*a*	<0.01 [e]	*a*	*a*	*a*
(17)	$\overline{O\cdot CH_2\cdot O\cdot CH{=}CH}$	*a*	<0.01	*a*	*a*	*a*

[a] Not determined. [b] Dehydro-dimer prepared in the Hg-sensitized photolysis of 1,3-dioxolan. [c] G.c.-m.s. analysis indicates a probable molecular weight of 146 or 148; *m/e* 73 (100%), *m/e* 45 (50%). [d] Prepared from butane-1,4-diol and formic acid (H. Laato, *Suomen Kemi*, 1965, **38b**, 76). [e] G.c. analytical difficulties with this product could have led to a low value. [f] Prepared from anthracene and vinylene carbonate (N. D. Field, *J. Amer. Chem. Soc.*, 1961, **83**, 3504).

The method of the internal standard was employed in the g.c. analyses. Reference material was commercially available or could be synthesized (see footnotes, Table 1 and 2), except for a few cases where assignments had to be made entirely on the basis of the mass spectra. Formic acid was determined titrimetrically. The dose rate of λ 185 quanta (solely photochemically active in these systems) was 4.6×10^{17} min^{-1} per 2 ml sample as measured by the ethanol

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[1] P. Naderwitz, H.-P. Schuchmann, and C. von Sonntag, *Z. Naturforsch.*, 1977, **32b**, 209.

[2] H.-P. Schuchmann and C. von Sonntag, *J.C.S. Perkin II*, 1976, 1408.

[3] H.-P. Schuchmann and C. von Sonntag, *Z. Naturforsch.*, 1977, **32b**, 205.

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[6] H.-P. Schuchmann and C. von Sonntag, *Tetrahedron*, 1973, **29**, 3351.

[7] H.-P. Schuchmann and C. von Sonntag, *Z. Naturforsch.*, 1975, **30b**, 399.

[8] B. C. Roquitte, *J. Phys. Chem.*, 1966, **70**, 2863.

[9] F. Weeke, E. Bastian, and G. Schomburg, *Chromatographia*, 1974, **7**, 163.

actinometer.[10] Total doses ranged from 2.3×10^{18} to 2.8×10^{19} quanta per sample, corresponding to conversions between *ca.* 0.04 and 0.5%. In this dose range product formation was linear with time. The quantum yields derived from the yield–dose plots are considered to be accurate to ±10% for the major products. Product formation was also measured as a function of temperature between 8 and 65 °C at conversions below 0.15%. The photolysis cell could be maintained at the desired temperature within ±1 °C.

TABLE 2

Photolysis (λ 185) of 2,2-dimethyl-1,3-dioxolan. Product quantum yields at various temperatures

		8 °C	20 °C	35 °C	50 °C	65 °C
(18)	H_2	*a*	0.002	*a*	*a*	*a*
(19)	CO	*a*	$<10^{-4}$	*a*	*a*	*a*
(20)	CO_2	0.066	0.078	0.083	0.095	0.103
(21)	CH_4	*a*	0.08	0.09	0.10	0.10
(22)	C_2H_4	*a*	0.18	0.16	0.15	0.14
(23)	C_2H_6	*a*	0.052	0.048	0.046	0.042
(24)	CH_2O	*a*	*a*	*a*	*a*	*a*
(25)	MeCHO	0.14	0.13	0.12	0.12	0.11
(26)	$\overline{CH_2CH_2O}$	0.12	0.11	0.10	0.10	0.09
(27)	Me_2CO	0.31	0.27	0.26	0.26	0.24
(28)	$Me_2\overline{CCH_2O}$	0.004	0.005	0.004	0.004	0.005
(29)	$MeCO_2Me$	0.12	0.12	0.10	0.10	0.09
(30)	$MeCO_2CH{=}CH_2$	0.010	0.009	0.008	0.008	0.008
(31)	$MeCO_2Et$	0.037	0.042	0.043	0.052	0.057
(32)	$MeCO_2Pr$	0.25	0.24	0.21	0.21	0.19
(33)	$Me\overline{CH{\cdot}O{\cdot}CMe_2{\cdot}O{\cdot}CH_2}$ [b]	0.01	0.01	0.01	0.01	0.01
(34)	$\overline{CH_2{\cdot}O{\cdot}CMe(Et){\cdot}O{\cdot}CH_2}$ [c]	*a*	$<10^{-3}$	*a*	*a*	*a*
(35)	$[\overline{O{\cdot}CMe_2{\cdot}O{\cdot}CH_2CH}]_2$ *meso* [d]	0.012	0.013	0.014	0.018	0.020
	(±) [e]	0.011	0.012	0.013	0.017	0.019
(36)	$(CH_2)_4(O_2CCH_3)_2$ [f]	4.5×10^{-3}	3.9×10^{-3}	3.3×10^{-3}	3.1×10^{-3}	2.5×10^{-3}

[a] Not determined. [b] Prepared from propylene glycol and acetone (*cf.* O. T. Schmidt, in ' Methods in Carbohydrate Chemistry,' eds. R. L. Whistler, M. L. Wolfrum, and J. N. BeMiller, Academic Press, New York, 1963, vol. II, p. 324). [c] Prepared from ethylene glycol and ethyl methyl ketone (M. J. Astle, J. A. Zaslowsky, and P. G. Lafyatis, *Ind. Eng. Chem.*, 1954, **46**, 787). [d] Prepared from *meso*-erythritol and acetone (A. B. Foster, M. H. Randall, and J. M. Webber, *J. Chem. Soc.*, 1965, 3388). [e] Assigned through g.c.-m.s. only. [f] Prepared from butane-1,4-diol and acetic anhydride.

A mixture of 1,3-dioxolan and di-t-butyl peroxide (v : v 10 : 1) was photolyzed at λ 254 and the yields at 20 and 50 °C of ethyl formate and dehydro-dimer were measured. Similarly, a mixture of 2-methyl-1,3-dioxolan and di-t-butyl peroxide was photolyzed and the CO_2 measured.

The molar extinction coefficients of both dioxolans in the liquid and vapour phase were determined in the wavelength region near 185 nm using a previously described procedure.[3]

RESULTS AND DISCUSSION

The dioxolans studied begin to absorb noticeably around 200 nm. Their molar extinction coefficients near 185 nm are plotted against the wavelength in Figures 1 and 2. Absorption sets in at shorter wavelengths than is the case for tetrahydrofuran and its methylated derivatives.[11] A similar behaviour is found when some open-chain acetals [2,3] are compared with open-chain ethers.

The quantum yields of the λ 185 photolysis products from both dioxolans are listed in Tables 1 and 2 as functions of temperature.

The proposed mechanism is given in the Scheme. It is concluded that in both dioxolans the main primary processes involve the rupture of the O(1)–C(5) bond [reactions (1)—(3)]. Moreover, it appears that several different processes are consecutive to C(5)–O(1) bond cleavage [reaction (2)], and that the extent to which reactions (1) and (3) occur cannot be established.

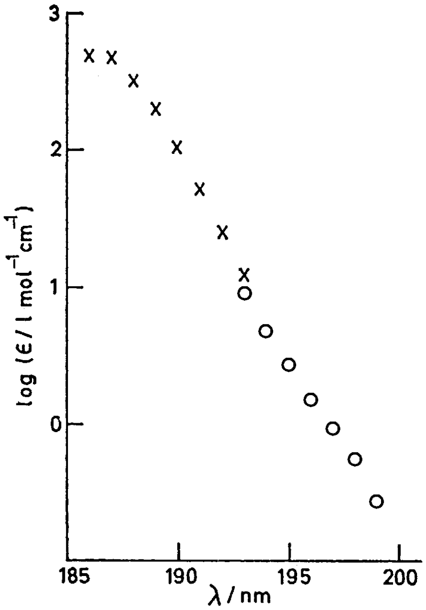

FIGURE 1 Molar extinction coefficient of 1,3-dioxolan near 185 nm: ○ = liquid and × = vapour

Reaction (11) is certainly possible for R = H [product: ethyl formate, (12)]; it seems less plausible for R = Me

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[10] C. von Sonntag and H.-P. Schuchmann, *Adv. Photochem.*, 1977, **10**, 80.

[11] N. Kizilkiliç, H.-P. Schuchmann, and C. von Sonntag, to be published.

[product: propyl acetate (32)]. The latter might also be formed in a cage reaction from radicals formed in reaction (12). The high quantum yield of (32) compared to other products containing the methyl unit, (21), (23), and (33), argues for a concerted mechanism such as reaction (11), or a cage reaction. On the basis of the difference of the C–C and C–H bond dissociation energies it is expected that the fragmentation reaction (12) occurs more readily with R = Me than with R = H. We believe that under our experimental conditions reaction (12) does not occur at all with the biradical derived from 1,3-dioxolan. Another subsequent event is cleavage of the C(2)–O(3) bond [reaction (13)]. Instead of the processes (2) and (13) occurring sequentially, however, a molecular elimination may occur [reaction (3)]. The birical $^{\bullet}CH_2-CH_2-O^{\bullet}$ may be involved in the formation of oxiran and acetaldehyde. The same products would also be obtained if the scission of the O(1)–C(2) bond were a primary process. Such scissions have been postulated in the open-chain acetals.[1-3] The quantum yields of the relevant products give a balance within experimental error for 2,2-dimethyl-1,3-dioxolan [$\phi(25) + (26) = \phi(27)$]. A similar balance for 1,3-dioxolan however could not be drawn up since the determination of formaldehyde by g.c. is impracticable and the wet analysis which is usually reliable could not be applied.

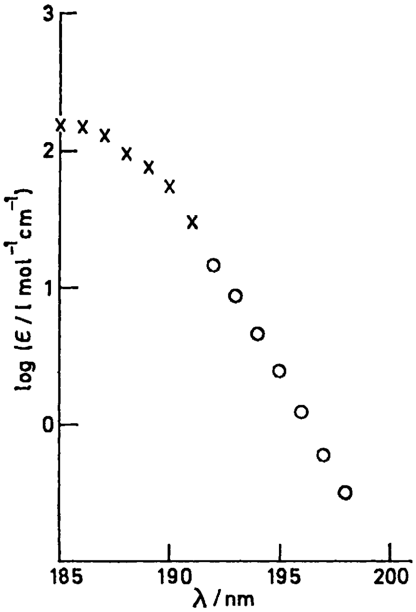
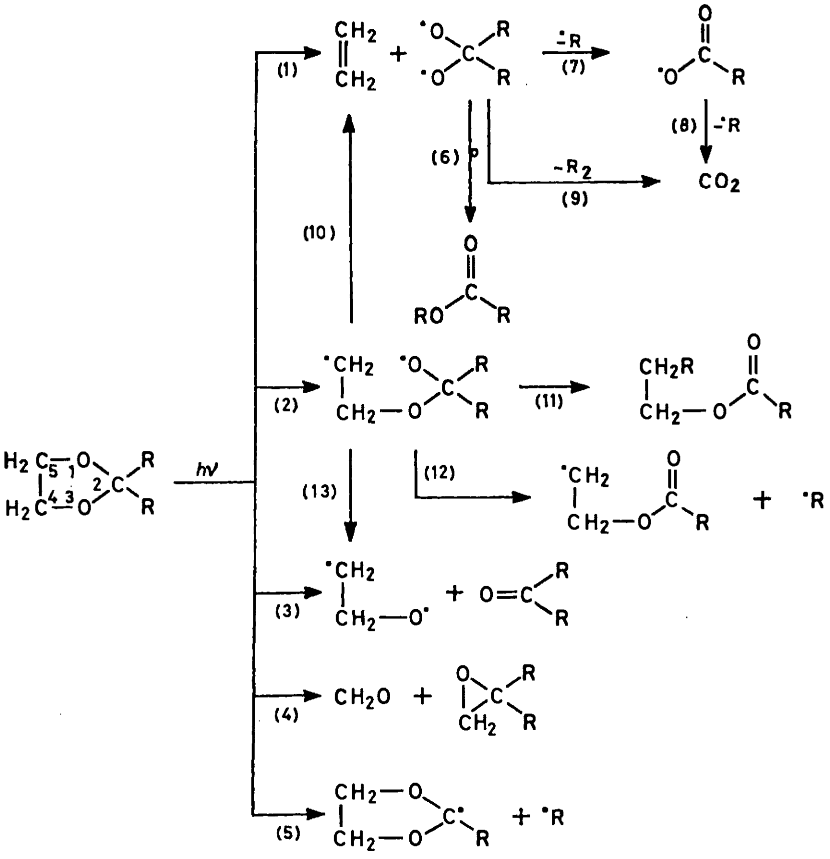
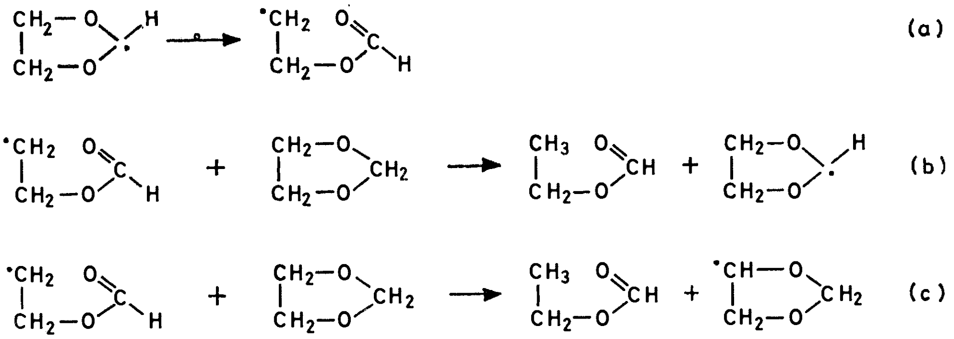


FIGURE 2 Molar extinction coefficient of 2,2-dimethyl-1,3-dixolan near 185 nm: ○ = liquid and × = vapour

A further family of products is derived from scission of the O(3)–C(4) bond [reaction (10)] following O(1)–C(5) bond cleavage [reaction (2)], and/or from the molecular process (1). It is thought that dioxirans or their equivalent biradicals might be the intermediates formed with ethylene. The dioxirans would then rearrange



SCHEME Primary processes in the photolysis (λ 185 nm) of liquid 1,3-dioxolan (R = H) and 2,2-dimethyl-1,3-dioxolan (R = Me) [reaction (6)] to formic acid (8) or methyl acetate (29), lose their C(2) substituents, and release CO_2. These substituents are probably lost either as $^{\cdot}CH_3$ or $^{\cdot}H$, [reaction (7) and (8) or C_2H_6 or H_2 [reaction (9)]. In the di-t-butyl peroxide-sensitized photolysis of 2-methyl-1,3-dioxolan where 2-methyl-1,3-dioxolan-2-yl radicals are estimated to be formed with a quantum yield of *ca.* 0.7, CO_2 was formed with a quantum yield of 0.01. Thus, it appears that the 1,3-dioxolan-2-yl radical may undergo fragmentation into ethylene and carboxyl (the latter giving rise to CO_2) with a low probability, in accordance with the finding that the CO_2 quantum yields from dioxolan and dimethyldioxolan are very similar while the two photolyses differ greatly as to the degree of involvement of the respective dioxolan-2-yl radicals. The fragmentation processes (7), (8), and (12) are probably the main source of the primary mono-radicals in these systems. Hydrogen abstraction from the substrate by these, as well as to a minor extent by the primary biradicals, leads to the dehydro-dimers *via* the 1,3-dioxolan-2-yl and the 2,2-dimethyl-1,3-dioxolan-4-yl radicals. In 1,3-dioxolan the dehydro-dimer yield combined with the yield of vinyl formate [ϕ(11) + (13) + (14) + (15) + (16) = 0.21] equals that of molecular hydrogen [ϕ(1) = 0.20]. This would argue against a major contribution of reaction (9) to CO_2 and H_2 formation if it is assumed that reactions (5) and (12) are of minor importance. In the case of 2,2-dimethyl-1,3-dioxolan it can be shown (see below) that reaction (5) may be neglected. While reaction (12) might play a role in the case of 2,2-dimethyl-1,3-dioxolan, it has been suggested above that this reaction is not likely under our experimental conditions with the unsubstituted dioxolan.



The 1,3-dioxolan-2-yl radical is prone to ring-opening. A radical chain is set up with ethyl formate as its product (reactions a and b). This explains the strong increase of its quantum yield with temperature. The fact that the yield of ethyl formate from the di-t-butyl peroxide-sensitized photolysis of 1,3-dioxolan at 50 °C is found to be four times greater than at 20 °C while the yield of one dehydro-dimer diminishes (the other staying about constant) serves as further proof that the 1,3-dioxolan-2-yl radical is the main precursor of ethyl formate in this system.

In agreement with the literature,[12,13] reactions (b) and (c) appear to be fast compared to reaction (a), since in the present systems it is from the dioxolanyl radicals that the dehydro-dimers are formed as the main radical combination products. No chain reaction is possible in the 1,2-dimethyldioxolan system. In both systems, the near absence of combination products of the precursors of the ethyl esters, the 2-acyloxyethyl radicals, suggests that they mostly abstract rather than combine.

The importance of reaction (4) cannot be gauged in the case of 1,3-dioxolan because it yields the same products as do reactions (3) and (13). However, the results from 2,2-dimethyl-1,3-dioxolan suggest that reaction (4) is unimportant [ϕ(28) = 0.005]. Scission of C–H bonds at C(3) and C(4) (not shown in the Scheme) are equally negligible [*cf.* ϕ(18) = 0.002]. All the identified products except carbon monoxide [ϕ(CO) = 0.014 from 1,3-dioxolan] are explained in a straightforward manner by the Scheme. The CO itself probably arises, as formulated [8] for the gas phase photolysis, from thermally excited intermediates which have escaped quenching in the liquid.

Because 2,2-dimethyl-1,3-dioxolan does not show a chain reaction it is possible to calculate quantum yields for the primary processes, or at least for several of them combined, on the basis of key products. Reactions (1) + (2) ⟶ (10) are given by ϕ(22) = 0.18. Reactions (2) ⟶ (11) and (2) ⟶ (12) are represented by ϕ[(30) + (31) + (32)] = 0.29. Reactions (3) and (2) ⟶ (13) are given by ϕ(27) or ϕ[(25) + (26)] $\simeq$ 0.26, and reaction (4) by ϕ(28) = 0.005. The value for ϕ [reaction (5)] is expected to be small (<0.01 since there is no trace of the 2-methyl-1,3-dioxolanyl radical). The total quantum yield of these primary processes is thus *ca.* 0.75. It is quite likely that the quantum yield of the sum of the primary processes is unity but that reclosure of the intermediate biradical [from reaction (2)] occurs. Recently the reclosure of a similar biradical has been found in the photolyses of *cis*- and *trans*-dimethyltetrahydrofuran.[11] The 1,3-dioxolan itself appears to follow routes similar to its dimethyl analogue but, as stated above, exact apportionment is not feasible.

A comparison between these dioxolans and some open-chain acetals studied previously [1-3] indicates that the

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[13] A. L. J. Beckwith and P. K. Tindal, *Austral. J. Chem.*, 1971, **24**, 2099.

cyclic dialkoxymethyl radicals undergo β-cleavage [reaction (a)] more easily than open-chain dialkoxymethyl radicals, to give the ester. With 1,1-dialkoxyalkyl radicals, the trend is towards increasing ease of β-cleavage, the higher the degree of branching of the alkyl radical eliminated.[14-17] A further route to esters not accessible to open-chain acetals is *via* the 1,5-biradical [reactions (11), (12), and (10) followed by (6)]. The possible intermediacy of dioxiran-like fragments [reactions (1) and (2) ⟶ (10)] in the 1,3-dioxolan photolyses may be the reason for their CO_2 production, in contrast to the open-chain acetals which yield none.

[7/1765 *Received, 6th October*, 1977]

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[17] S. Steenken, H.-P. Schuchmann, and C. von Sonntag, to be published.