Radiation Chemistry of Acetals. Part 1. Photolysis (λ 185 nm) of Formaldehyde Dimethyl Acetal in the Liquid Phase

By **Heinz-Peter Schuchmann and Clemens von Sonntag,*** Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim a.d. Ruhr, W. Germany

In the photolysis (λ 185 nm) of liquid formaldehyde dimethyl acetal the following products are formed (quantum yields in parentheses): hydrogen (0.04), methane (0.22), ethane (0.01), formaldehyde (>0.15), methanol (0.35), methyl formate (0.17_5), dimethyl ether (0.13), methyl ethyl ether (0.02_5), acetaldehyde dimethyl acetal (0.04), formaldehyde methyl ethyl acetal (0.04), 1,2-dimethoxyethane (0.025), methoxyacetaldehyde dimethyl acetal (0.07_4), formaldehyde methoxyethyl methyl acetal (0.05_4), and dehydro-dimers (0.1). It is concluded that the photolysis is largely governed by reactions (i)—(v). Reaction (i) and (iv) include cage disproportionation processes.

$$H_2C(OCH_3)_2 \xrightarrow{h\nu} HCOOCH_3 + CH_4 \qquad \phi = 0.18 \qquad \text{(i)}$$

$$H_2C(OCH_3)_2 \xrightarrow{h\nu} CH_3OCH_2O^{\bullet} + {}^{\bullet}CH_3 \qquad \phi = 0.17 \qquad \text{(ii)}$$

$$H_2C(OCH_3)_2 \xrightarrow{h\nu} CH_3OCH_2^{\bullet} + {}^{\bullet}OCH_3 \qquad \phi = 0.18 \qquad \text{(iii)}$$

$$H_2C(OCH_3)_2 \xrightarrow{h\nu} CH_2O + CH_3OCH_3 \qquad \phi = 0.13 \qquad \text{(iv)}$$

$$H_2C(OCH_3)_2 \xrightarrow{h\nu} H^{\bullet} + {}^{\bullet}CH_2OCH_2OCH_3 + H\dot{C}(OCH_3)_2 \qquad \phi = 0.04 \qquad \text{(v)}$$

THE photolysis of saturated compounds is attracting increasing attention. Alkanes absorb in the vacuum u.v. region only, but oxygen-containing saturated compounds such as alcohols, ethers, and acetals show absorption in the 200 nm region. This first absorption band is thought to be due to an $n \longrightarrow \sigma^*$ transition.[1]

The low pressure Hg arc emits two major lines, one at 185, the other at 254 nm. The former lies near to the first absorption maximum of these compounds whereas the latter is either not absorbed by these systems or contributes only negligibly to their photolysis.

The photolysis of saturated straight chain acetals has not been investigated prior to this study. However, the gas-phase photolysis using a medium pressure Hg arc (active λ 190—200 nm) of the cyclic acetal 1,3-dioxolan has been studied by Roquitte[2] who found that two primary processes are important, namely its decomposition into formaldehyde, CO, methyl, and $H^{\bullet}$, as well as into ethylene, CO_2, and hydrogen. The photolytic behaviour of cyclic compounds is often different from that of their straight-chain counterparts, and one does not expect a complete analogy between formaldehyde dimethyl acetal and 1,3-dioxolan. There may be similarities between the photolysis of the former and open-chain ethers. The photolysis of some representatives of the latter class has recently been studied in this laboratory.[3-9]

EXPERIMENTAL

Formaldehyde dimethyl acetal (Fluka) was fractionally distilled but could not be completely freed of methanol. The material used in the photolyses contained *ca.* 100 p.p.m. of methanol which did not interfere. The yield–dose curves of methanol were linear, with an intercept. The molar extinction coefficient of oxygen-free formaldehyde dimethyl acetal was determined on a Cary model 17 spectrograph. Near 185 nm the extinction of the vapour contained in a 1 cm Suprasil QS cell was measured. The evacuated cell was connected to a bulb with the acetal kept at 0°, and left

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[1] J. G. Calvert and J. N. Pitts, jun., 'Photochemistry,' Wiley, New York, 1966.

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

[3] C. von Sonntag, H.-P. Schuchmann, and G. Schomburg, *Tetrahedron*, 1972, **28**, 4333.

[4] H.-P. Schuchmann and C. von Sonntag, *Tetrahedron*, 1973, **29**, 1811.

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

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

[7] R. Ford, H.-P. Schuchmann, and C. von Sonntag, *J.C.S. Perkin II*, 1975, 1338.

[8] S. Steenken, H.-P. Schuchmann, and C. von Sonntag, *J. Phys. Chem.*, 1975, **79**, 763.

[9] H.-P. Schuchmann, C. von Sonntag, and D. Schulte-Frohlinde, *J. Photochem.*, 1974—1975, **3**, 267.

to equilibrate. The pressure is then 130.7 Torr,[10] and the acetal concentration in the cell at 26° is 7.05×10^{-3}M. At wavelengths >189 nm the extinction coefficient of the liquid could be determined from a 0.010 cm layer using a 0.090 cm Suprasil spacer in a 0.100 cm cell.

The photolyses were carried out at 185 nm as previously described.[3-5] Dosimetry was performed with the ethanol actinometer [11-13] based on a H_2 quantum yield [13] of 0.4. Dose rates ranged from 1.5 to 5.0×10^{17} quanta min^{-1} absorbed in a 2 ml sample (irradiated surface 2 cm^2). All products were analysed by g.l.c. using liquid or vapour injection. All products except the two dehydro-dimers (17) and (18) were calibrated by measuring the g.l.c. response of a known amount of pure reference material. Products (17) and (18) were assumed to have the same molecular g.l.c. response as the available dehydro-dimer (16) [glyoxal bis(dimethyl acetal)]. The products hydrogen, methane, ethane, and dimethyl ether were analysed by scrubbing the irradiated sample.[14] G.l.c. details and sources of reference compounds are given in Table 1. G.l.c. peaks were assigned with the help of mass spectrometry and of authentic reference materials, purified by fractionation or preparative g.l.c. if required.

TABLE 1

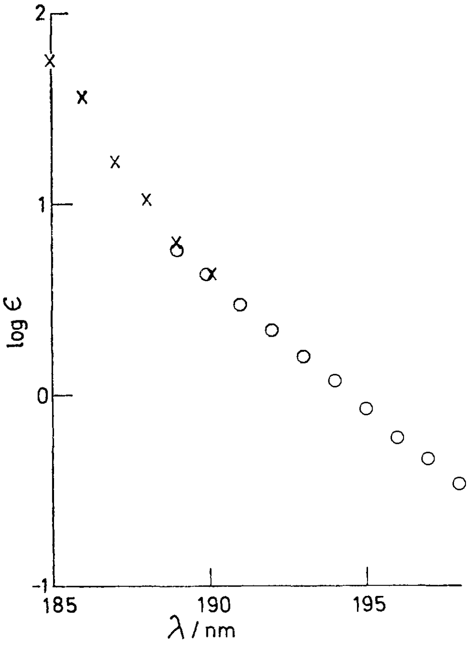
Retention times of products. Sources of reference compounds

	Relative retention time		Source
H_2	2.5[a]		
CO	5.5[b]		
CO_2	7.0[c]		
CH_4	2.8[d]	1.0[e]	
C_2H_6	3.8[d]	1.9[e]	
CH_2O		4.5[e]	Merck
CH_3OCH_3	11.2[d]	0.17[f]	Matheson
$C_2H_5OCH_3$		0.34[f]	*h*
$CHO{-}OCH_3$		0.93[f]	Fluka
$CH_2(OCH_3)_2$	1.00[g]	1.00[f]	Fluka
$CH_2(OCH_3)OC_2H_5$	1.35[g]	1.8[f]	*i*
$CH_3CH(OCH_3)_2$	1.51[g]	1.8[f]	Fluka
CH_3OH		2.2[f]	Merck
$CH_3OCH_2CH_2OCH_3$		4.1[f]	Merck
$CH_3OCH_2CH(OCH_3)_2$		15.2[f]	Aldrich
$CH_2(OCH_3)OCH_2CH_2OCH_3$		18.0[f]	*k*
$(CH_3O)_2CH{-}CH(OCH_3)_2$		26.6[f]	*l*
$(CH_3O)_2CH{-}CH_2OCH_2OCH_3$		31.2[f]	*m*
$CH_3OCH_2OCH_2CH_2OCH_2OCH_3$		34.4[f]	*m*

[a] Elution time in min. Column: active coal; 4 m × $\frac{1}{8}$ in. o.d.; 23°; 28 ml Ar min^{-1}. [b] Elution time in min. Column: active coal; 1 m × $\frac{1}{8}$ in o.d.; 50°; 55 ml He min^{-1}. [c] Elution time in min. Column combination: Porapak Q 100—120 mesh; 1 m × $\frac{1}{8}$ in o.d.; plus molecular sieve 5Å 80—100 mesh; 0.8 m × $\frac{1}{4}$ in o.d.; 50°; 11 ml He min^{-1}. [d] Elution time in min. Column: Porapak N 100—120 mesh; 3 m × $\frac{1}{8}$ in o.d.; 140°; 11 ml Ar min^{-1}. [e] Elution time in min. Column: Porapak N 100—120 mesh; 2 m × $\frac{1}{8}$ in o.d.; 115°; 9 ml Ar min^{-1}. [f] Capillary column: Marlophen 814; 100 m glass; 0.25 mm i.d.; temperature programmed 20 min 70°, 70—120° rate 4° min^{-1}; carrier gas H_2, 14.7 lb in^{-2}. [g] Capillary column: Oxydipropiononitrile; 100 m stainless steel; 0.25 mm i.d.; 70°; carrier gas Ar, 25 lb in^{-2}. [h] From the sodium alkoxide and methyl iodide. [i] Through partial transacetalization of formaldehyde diethyl acetal with methanol; catalyst toluene-*p*-sulphonic acid.[15] [k] Through partial transacetalization of formaldehyde dimethyl acetal with methoxyethanol; catalyst toluene-*p*-sulphonic acid.[15] [l] From glyoxal sulphate [16] and methanol.[17] [m] From irradiation at 254 nm of a mixture of formaldehyde dimethyl acetal and di-t-butyl peroxide (4 : 1).

RESULTS AND DISCUSSION

Formaldehyde dimethyl acetal is transparent in the near u.v., and absorption sets in at *ca.* 200 nm. The absorption coefficient at 185 nm is only 55 l mol^{-1} cm^{-1} (Figure), which is quite low by comparison with those of simple saturated ethers [4-6] which are usually between 200 and 3 000 l mol^{-1} cm^{-1} at this wavelength. Of the oxygen-containing saturated compounds only alcohols as neat liquids have such low extinction coefficients (ϵ_{185} <100 l mol^{-1} cm^{-1}).[18]



Molar extinction coefficient of formaldehyde dimethyl acetal between 185 and 198 nm: ×, vapour; ○, liquid

The yield of the products (Table 2) was directly proportional to the dose at conversions between 0.02 and 0.2%. Quantum yields were calculated based on $\phi(H_2) = 0.4$ for the Farkas actinometer, 5M ethanol in water.[11-13] Photolysis was negligible when the 185 nm line was cut off with a Vycor quartz platelet which is transparent to 254 nm light. Experimental errors are thought to be within 10% except for the case of formaldehyde. Polymerization tends to occur, especially when formaldehyde is formed as a major product. In this system only its volatile fraction could be analysed.

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[10] E. R. Nicolini, *Ann. Chim. Phys.*, 1949, **6**, 597.

[11] L. Farkas and Y. Hirshberg, *J. Amer. Chem. Soc.*, 1937, **59**, 2450.

[12] F. S. Dainton and P. Fowles, *Proc. Roy. Soc.*, 1965, *A*,**287**, 295.

[13] C. von Sonntag, *Z. phys. Chem.* (*Frankfurt*), 1970, **69**, 292.

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

[15] H. Meerwein, in 'Methoden der Organischen Chemie,' Vol. VI/3, Oxygen Compounds, Part 3, ed. E. Müller, Thieme Verlag, Stuttgart, 1965, p. 201.

[16] P. Ruggli and E. Henzi, *Helv. Chim. Acta*, 1929, **12**, 364.

[17] H. Fiesselmann and F. Hörndler, *Chem. Ber.*, 1954, **87**, 908.

[18] J. Barrett, A. L. Mansell, and M. F. Fox, *J. Chem. Soc.* (*B*). 1971, 173.

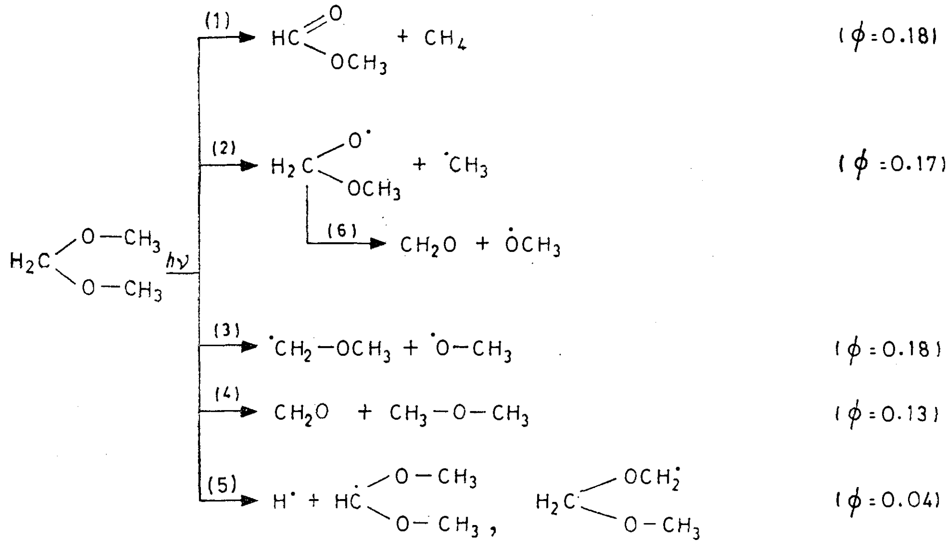
Spectrophotometric methods [19] such as the chromotropic acid and the Hantzsch reactions cannot be applied because formaldehyde dimethyl acetal itself gives a positive reaction. A reasonable material balance ($C_3H_{8.05}O_{1.99}$) is obtained on the basis of the products and their quantum yields if $\phi(CH_2O)$ is assumed to be *ca.* 0.3.

TABLE 2

Photolysis (185 nm) of liquid deaerated formaldehyde dimethyl acetal (15°). Products and quantum yields

No.	Product	Quantum yield
(1)	H_2	0.04
(2)	CH_4	0.22
(3)	CO	<0.002
(4)	C_2H_6	0.01
(5)	CH_2O	>0.15
(6)	CH_3OH	0.35
(7)	CO_2	$0(<10^{-4})$
(8)	CH_3OCH_3	0.13
(9)	$CH_3OC_2H_5$	0.02_5
(10)	$HCOOCH_3$	0.17_5
(11)	$CH_3CH(OCH_3)_2$	0.04
(12)	$CH_2(OCH_3)OC_2H_5$	0.04
(13)	$CH_3OCH_2CH_2OCH_3$	0.02_5
(14)	$CH_3OCH_2CH(OCH_3)_2$	0.07_4
(15)	$CH_2(OCH_3)OCH_2CH_2OCH_3$	0.05_4
(16)	$(CH_3O)_2CHCH(OCH_3)_2$	0.02
(17)	$CH_3OCH_2OCH_2CH(OCH_3)_2$	0.04
(18)	$CH_3OCH_2OCH_2CH_2OCH_2OCH_3$	0.04

The Scheme shows the major primary processes as derived from the products and their quantum yields whereby cage disproportionation processes could not be distinguished from the molecular elimination in this system. The quantum yield of reaction (1) is represented (see below) by ϕ(methyl formate) *ca.* 0.18. Besides being formed in reaction (1), some methane is also generated by hydrogen abstraction by methyl radicals [reaction (2)].



SCHEME 1 Primary processes and their quantum yields in the 185 nm photolysis of liquid formaldehyde dimethyl acetal

On the basis of all products having methyl radicals as precursors [$\phi(^{\cdot}CH_3) = \phi(2) - \phi(10) + 2\phi(4) + \phi(9) + \phi(11) + \phi(12) = 0.17$] the quantum yield of reaction (2) is estimated at *ca.* 0.17. The oxyl radical from reaction (2) might fragment into formaldehyde and a methoxyl radical [reaction (6)], or abstract a hydrogen atom from the starting material. Either reaction eventually leads to methanol, formaldehyde, and substrate radicals. The methoxyl radicals, rather than undergoing combination reactions with other radicals, abstract hydrogen from the starting material. This reaction is expected to have a high rate constant as the known value of *k* for the reaction of methoxyl with methanol, 5×10^5 l mol^{-1} s^{-1}, indicates.[20] The process competing with reaction (6) leads to formaldehyde methyl hemiacetal which is expected to decompose into its components under the present conditions.

A further source of methanol is reaction (3) followed by hydrogen abstraction from the substrate by methoxyl. Its quantum yield can be derived by either subtracting the quantum yield of reaction (2) from the methanol yield [giving 0.18 for ϕ of reaction (3)], or by adding the quantum yields of all products containing the structural element $^{\cdot}CH_2OCH_3$ except dimethyl ether [$\phi(^{\cdot}CH_2OCH_3) = \phi(9) + 2\phi(13) + \phi(14) + \phi(15) = 0.20_3$], arriving at a similar yield. The formation of dimethyl ether appears to be largely due to the molecular fragmentation process (4). Hydrogen abstraction by the $^{\cdot}CH_2OCH_3$ radical from the acetal appears to contribute only little to dimethyl ether formation, as indicated by the independence of its combination product quantum yields from the dose rate. Also, its complement $^{\cdot}OCH_3$ [in reaction (3)] is already fully accounted for by the above considerations. Thus ϕ of reaction (4) can be given by $\phi(CH_3OCH_3) = 0.13$. The formaldehyde in reaction (4) appears to be derived from the methoxy groups as is indicated by photolysis experiments with pivaldehyde dimethyl acetal (un-

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[19] B. Kakáč and Z. J. Vejdělek, 'Handbuch der photometrischen Analyse organischer Verbindungen,' Verlag Chemie, Weinheim, 1974, p. 257.

[20] D. H. Ellison, G. A. Salmon, and F. Wilkinson, *Proc. Roy. Soc.*, 1972, *A*, **328**, 23.

published results). Reaction (5) is of little importance. Its quantum yield is given by $\phi(H_2) = 0.04$ because of the high abstractive power of the hydrogen atoms which have no chance of undergoing combination reactions with other radicals in this system.

Acetal radicals are of varying stability.[21,22] The structural analogues of $^{\bullet}CH_2OCH_2OCH_3$ have been found to yield carbonyl compounds and alkoxyalkyl radicals, the analogues of $^{\bullet}CH(OCH_3)_2$ esters and alkyl radicals.[23] Similar radicals from 1,3-dioxolans and 1,3-dioxan are reported [24] to be stable towards β-cleavage in an aqueous medium, whereas radicals from cyclic acetals such as α-alkoxytetrahydropyrans on rearrangement give rise to lactones and/or esters.[25-27] Indeed, the formaldehyde dimethyl acetal radical does not fragment at room temperature as shown by e.s.r.[28] Nevertheless it seemed desirable to check whether process (1) was indeed the only route to methyl formate, or whether fragmentation of the acetal radical $^{\bullet}CH(OCH_3)_2$ contributed to its formation. The molecular nature of methyl formate formation was established by the fact that its quantum yield is independent of the dose rate. A series of experiments was carried out at different dose rates ranging from 0.15 to 0.48×10^{18} quanta min^{-1}. The only products to show a significant decline in quantum yield on decreasing the dose rate were the methyl radical combination products (9), (11), and (12) [gaseous products, *e.g.* (4), were not measured in this particular experiment]; the quantum yields of all other radical combination products such as those involving only radicals $^{\bullet}CH_2OCH_3$, $^{\bullet}CH_2OCH_2OCH_3$, and $^{\bullet}CH(OCH_3)_2$ did not change. This is as expected. Methyl radicals disappear by both hydrogen abstraction and combination and a lowering of the steady-state radical concentration disfavours combination. The other radicals mentioned are not expected to react by hydrogen abstraction but solely by combination, and the independence of their combination product quantum yields proves that they are stable with respect to fragmentation under the present conditions.

The possibility that the substrate radical $^{\bullet}CH_2OCH_2OCH_3$ might fragment into formaldehyde and $^{\bullet}CH_2OCH_3$, was checked in a separate experiment. When di-t-butyl peroxide was photolysed at 254 nm in formaldehyde dimethyl acetal at a concentration and a quantum flux which gave rise to substrate radicals at a steady-state concentration even lower than in the 185 nm experiments, dehydro-dimers [products (16)—(18)] were produced in high yields, but no products derived from $^{\bullet}CH_2OCH_3$ [products (13)—(15)] were found. This result argues against a contribution from acetal radicals to the $^{\bullet}CH_2OCH_3$ yield.

Reactions (2) and (4) are reminiscent of the predominant process in the gas-phase photolysis [2] of 1,3-dioxolan, the generation of formaldehyde and of the precursor of CO, $^{\bullet}CH_3$, and $^{\bullet}H$. The process giving ethylene, CO_2, and H_2 has no analogy in the present work where CO_2 is absent. Processes (1)—(3) and (5) but not (4) (Scheme) are generally similar to those encountered in the photolyses of straight-chain ethers. In methyl n-propyl ether [6] and t-butyl methyl ether the formation of formaldehyde is marginal which means that a process corresponding to (4) (Scheme) is unimportant.

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[21] M. J. Perkins and B. P. Roberts, *J.C.S. Perkin II*, 1975, 77.

[22] I. Rosenthal and D. Elad, *J. Org. Chem.*, 1968, **33**, 805.

[23] L. P. Kuhn and C. Wellmann, *J. Org. Chem.*, 1957, **22**, 774.

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

[25] E. S. Huyser, *J. Org. Chem.*, 1960, **25**, 1820.

[26] T. Yamagishi, T. Yashimoto, and K. Minami, *Tetrahedron Letters*, 1971, 2795.

[27] C. Bernasconi and G. Descotes, *Compt. rend.*, 1975, **280C**, 469.

[28] S. Steenken, personal communication.