Photolytic Oxidation of Ethylene Glycol Dimethyl Ether and Related Compounds by Aqueous Hypochlorite

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The photochemical oxidation of ethylene glycol dimethyl ether (EDE) and related substrates by aqueous sodium hypochlorite has been studied. In the presence of a large excess of hypochlorite, EDE is completely photolysed to give CO_2 and H_2O. On the other hand, irradiation of an equimolar mixture of the substrate and aqueous hypochlorite gives CH_3OH, HCHO, HCOOH, $CH_3OCH_2CH_2OH$, CH_3OCH_2CHO, CH_3COOH, and a trace of $CHCl_3$, which is the only chlorine-containing product. The photo-oxidation of the other substrates gives analogous products.

POLYETHERS, especially polyethylene glycol derivatives, are widely used as surfactants; their contamination of water can lead to serious pollution problems. Removal of surfactants by biochemical or physical (*i.e.* adsorption) methods is often insufficient especially in the case of polyethers.

Inoue and his co-workers have reported the photo-oxidation of ethylene glycol dimethyl ether (EDE) in the presence of triplet oxygen [1] and $FeCl_3$.[2] The u.v.

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[1] H. Inoue, K. Tamaki, and E. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1966, **69**, 645.

[2] H. Inoue, K. Tamaki, N. Komakine, and E. Imoto, *Bull. Chem. Soc. Japan*, 1966, **39**, 1577.

photolysis of neat ethylene glycol monomethyl ether (EME) [3] and diallyl ethers [4] have also been reported.

Recently, an effective industrial process was developed for the photo-oxidative removal of several organic contaminants in waste water by aqueous alkaline hypochlorite [5] by which most organic materials are completely decomposed to CO_2, HCl, and H_2O. However, there is no detailed information about the intermediate products and reaction mechanism for this hypohalite oxidation. Some products may cause secondary pollution in this process.

Recently, we reported the photo-oxidation of alkyl benzenesulphonates by aqueous hypochlorite in which alkylbenzene, alkylphenol, aralkyl alcohol, and aralkylaldehyde were intermediate products.[6] The present paper is an attempt to examine the intermediate products and mechanism of u.v. photolysis of EDE as a model compound for polyethylene glycols in the presence of aqueous sodium hypochlorite. In addition, photo-oxidation of related substrates such as EME, ethylene glycol (EG), diethylene glycol (DEG), its monomethyl ether (DEME), and dimethyl ether (DEDE) were studied along with EDE.

RESULTS AND DISCUSSION

Irradiation of an aqueous mixture of EDE and 25-fold equivalents of sodium hypochlorite gave, after complete disappearance of hypochlorite, only CO_2 (*ca.* 90%). No organic compounds were detected by g.l.c. In other words, EDE was oxidised almost completely to CO_2 and H_2O.

TABLE 1

Yields of photo-oxidation products from EDE, EME, and EG by aqueous NaOCl at 17° [a,b]

	$CH_3OCH_2CH_2OCH_3$ (EDE)	$CH_3OCH_2CH_2OH$ (EME)	$HOCH_2CH_2OH$ (EG)
[Substrate]$_0$/mM	220	225	219
[NaOCl]$_0$/mM	225	225	225
t/min	30	30	75
Conversion (%)	50.2	42.8	23.1
Products [c]	Yield [d] (%)	Yield [d] (%)	Yield [d] (%)
EME	10.8 (14.5)		
EG	2.3 (4.6)	2.8 (4.2)	
CH_3OCH_2CHO	0.7 (0.9)	1.0 (1.0)	
CH_3CH_2OH		Trace	15.4 (15.4)
CH_3COOH	1.8 (3.6)	6.4 (9.7)	Trace
CH_3OH	20.4 (81.5)	16.0 (48.0)	Trace
HCHO	3.6 (14.5)	7.3 (21.8)	19.8 (39.5)
HCOOH	3.7 (15.0)	11.8 (35.4)	60.5 (121.0)
Total yield (%)	43.3	45.3	95.7

[a] Conversion of NaOCl *ca.* 100%. [b] At pH >12. [c] Other minor products are: $HOCH_2CHO$, $CH_3OCH_2CH_2OOCH$, $CH_3OCH_2CH_2OCH_2OH$, CH_3CHO, $CHCl_3$, CH_4, and C_2H_6 from EDE; $HOCH_2CHO$, CH_3CHO, $CHCl_3$, CH_4, and C_2H_6 from EME; $HOCH_2CHO$ from EG. [d] Yields are based on the carbon atoms of the consumed substrate. Values in parentheses are ordinary molar yields based on the consumed substrate.

On the other hand, photolysis of an aqueous mixture of equimolar EDE and NaOCl gave little CO_2 (only a few percent), and many organic products were detected; *e.g.*, EME, EG, methoxyacetaldehyde, acetic acid, methanol, formaldehyde, and formic acid were obtained as main products as shown in Table 1. Further, some other minor products were also produced. Identification was carried out by g.l.c. and g.l.c.–m.s. The mass spectral fragmentations are given in Table 3. A little methane and ethane but not oxygen were detected as

TABLE 2

Yields of photo-oxidation products from DEDE, DEME, and DEG by aqueous NaOCl at 17° [a,b]

	$CH_3O(CH_2CH_2O)_2CH_3$ (DEDE)	$CH_3O(CH_2CH_2O)_2H$ (DEME)	$HO(CH_2CH_2O)_2H$ (DEG)
[Substrate]$_0$/mM	118	113	115
[NaOCl]$_0$/mM	220	220	225
t/min	20	20	20
Conversion (%)	57.7	56.0	40.4
Products [c]	Yield [d] (%)	Yield [d] (%)	Yield [d] (%)
DEME	4.3 (5.1)		
DEG	2.2 (3.3)	1.1 (1.2)	
EME	8.6 (17.2)	9.4 (15.6)	
EG	6.5 (20.5)	17.0 (42.6)	45.2 (90.4)
CH_3CH_2OH	1.5 (4.6)	5.3 (13.3)	5.7 (11.4)
CH_3COOH	Trace	7.3 (18.2)	31.7 (62.4)
CH_3OH	8.4 (50.4)	5.7 (28.6)	
HCHO	3.1 (18.4)	2.8 (14.2)	4.6 (18.3)
HCOOH	0.8 (4.5)	6.2 (30.8)	7.0 (28.0)
Total yield (%)	35.7	54.8	93.7

[a] Conversion of NaOCl *ca.* 100%. [b] At pH >12. [c] Other minor products are: CH_3OCH_2CHO, $CH_3CH_2OCH_2CH_2OH$, $HOCH_2CHO$, CH_3CHO, $CHCl_3$, CH_4, and C_2H_6 from DEDE; CH_3OCH_2CHO, $CH_3CH_2OCH_2CH_2OH$, $HOCH_2CHO$, CH_3CHO, $CHCl_3$, CH_4, and C_2H_6 from DEME; $HOCH_2CHO$, C_2H_6, and $CHCl_3$ from DEG. [d] Yields are based on the carbon atoms of the consumed substrate. Values in parentheses are ordinary molar yields based on the consumed substrate.

TABLE 3

G.l.c.–m.s. analysis of products from the photo-oxidation of EDE and related compounds by aqueous NaOCl at 17° [a,b]

Parent ion peak (*m*/*e*)	Fragment ion peaks (*m*/*e*)	Compound
106	91, 89, 73, 70, 61, 59, 45, 43, 31, 29, 18	(27)
104	60, 59, 58, 57, 47, 46, 45, 31, 29, 15	$CH_3OCH_2CH_2OOCH$
	85, 83, 73, 59, 45	$CHCl_3$
90	60, 59, 58, 57, 47, 46, 45, 31, 29, 15	EDE
76	58, 47, 46, 45, 44, 43, 31, 29, 15	EME
62	61, 46, 45, 44, 33, 31, 29, 15	EG
	73, 60, 46, 45, 44, 43, 31, 29, 15	CH_3OCH_2CHO
46	45, 31, 30, 29, 18	CH_3CH_2OH
46	45, 44, 29, 28, 18	HCOOH
44	43, 31, 29, 18, 15	CH_3CHO
32	31, 30, 29	CH_3OH

[a] [Substrate]$_0$ = 1.2M; [NaOCl]$_0$ = 1.1M. [b] At pH >12.

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

[4] Y. Ogata, K. Takagi, and I. Ishino, *Tetrahedron*, 1970, **26**, 2703.

[5] Y. Kojima, *PPM*, 1973, 42.

[6] N. Nakamura and Y. Ogata, *Bull. Chem. Soc. Japan*, 1977, **50**, 2396.

gaseous products. Similarly, the main products from the photo-oxidation of EME, EG, DEG, DEME, and DEDE were also studied in comparison with those from EDE. Analogous products were obtained as shown in Tables 1 and 2.

The effect of irradiation time on the photolysis of EDE and DEDE was examined with five-fold equivalents of NaOCl with EDE and ten-fold equivalents of NaOCl with DEDE (Figures 1 and 2). With larger excess of NaOCl, formic acid becomes the main product, the yield of methanol being lower. There is no significant interconversion between products, since all yields of products increase as the reaction proceeds, *i.e.* they were formed directly from the substrates.

The u.v. spectra of aqueous alkaline sodium hypochlorite shows strong absorption at 292 nm (ε 400 l mol^{-1} cm^{-1}), and the excitation of substrates (EDE and others) is negligible under our conditions on account of the transparency of the reaction system at over 230 nm. Hence the reaction is initiated by the excitation of NaOCl followed by attack of the species formed on the ground-state substrates.

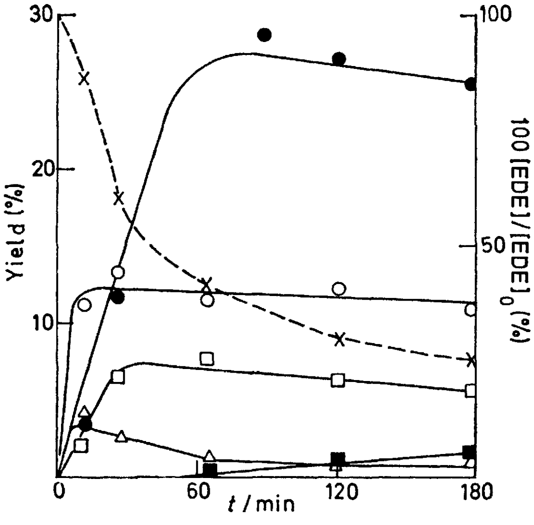

FIGURE 1 Effect of irradiation time on yields of products from the photolysis of EDE by aqueous NaOCl at 17°: □, EME; ■, EG; △, CH_3OCH_2CHO; ○, CH_3OH; ●, HCOOH; ×, EDE. $[EDE]_0$ 187mM, $[NaOCl]_0$ 956mM; pH >12; conversion of NaOCl after 3 h, 86.0%; all yields based on substrate consumed

Buxton and Subhani reported the photodecomposition of alkaline aqueous hypochlorite[7] to give O(^3P), O(^1D), O$^-$, Cl, and Cl$^-$ [equations (1)—(3)].

$$\mathrm{ClO^-} \xrightarrow{h\nu} \begin{cases} \mathrm{Cl^- + O(^3\mathit{P})} & (1) \\ \mathrm{Cl + O^-} & (2) \\ \mathrm{Cl^- + O(^1\mathit{D})} & (3) \end{cases}$$

The quantum yields (φ) of equations (1)—(3) at 313 nm are ϕ_1 0.075, ϕ_2 0.127, and ϕ_3 0.02 respectively. Some of the products may be hydrogen abstractors which initiate radical chain reactions. Excited-state atomic oxygen, O(^1D), reacts with water[8] to produce two hydroxyl radicals [equation (4)]. Oxide radical anion, O$^-$, gives

$$\mathrm{O(^1\mathit{D}) + H_2O \longrightarrow 2HO\cdot} \qquad (4)$$

a hydroxyl radical and a hydroxide ion in water;[9] thus O(^1D) and O$^-$ have similar behaviour. At higher pH region, O$^-$ is the predominant and more important oxidising species, since $-\log K_5$ is 11.9, where K_5 is an

$$\mathrm{O^- + H_2O \rightleftharpoons OH^- + HO\cdot} \qquad (5)$$

equilibrium constant for equation (5).

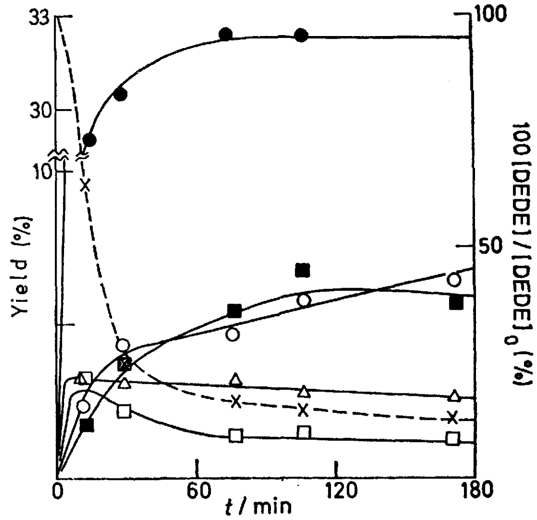

FIGURE 2 Effect of irradiation time on yields of products from the photolysis of DEDE by aqueous NaOCl at 17°: △, DEME; ■, EME; □, CH_3CH_2OH; ○, CH_3OH; ●, HCOOH; ×, DEDE. $[DEDE]_0$ 103mM, $[NaOCl]_0$ 947mM; pH >12; conversion of NaOCl after 3 h, 70.3%; all yields based on substrate consumed

The reactivities of HO•, O$^-$, and O(^3P) against ethanol, *i.e.*, the relative rate constants of hydrogen

$$\mathrm{R^1OCH_2CH_2OCH_2R^2}$$
(1)

a; $R^1 = H$, $R^2 = H$ (EME)
b; $R^1 = CH_3$, $R^2 = H$ (EDE)
c; $R^1 = H$, $R^2 = CH_2OH$ (DEG)
d; $R^1 = H$, $R^2 = CH_2OCH_3$ (DEME)
e; $R^1 = CH_3$, $R^2 = CH_2OCH_3$ (DEDE)
f; $HOCH_2CH_2OH$ (EG)

atom abstraction from ethanol decrease in the order: $k_{(\mathrm{OH})}$[10] : $k_{(\mathrm{O^-})}$[11] : $k_{[\mathrm{O}(^3P)]}$[12] = 20 : 9 : 1. Though O(^1D) is a highly reactive species, the effect of O(^1D) on organic

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[10] M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc.* (*B*), 1966, 742.

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compounds is little known.[13] Atomic chlorine can also be a hydrogen atom abstractor.[14]

The reaction may be initiated by hydrogen atom abstraction by these species from substrates [equations (6) and (7)]. Radicals thus formed (2)—(4) may undergo α- and/or β-fission (C–O fission) to give products and/or other radicals [equations (8)—(10)]. The products and radicals produced in equations (8)—(10) may undergo further reactions [equations (11)—(19)] to give fairly stable products [(6), (9), and (12)—(19)], which were all identified except for species in square brackets which were easily polymerised.

$$\underset{(1)}{\mathrm{R^1OCH_2CH_2OCH_2R^2}} \xrightarrow{-\mathrm{H}} \underset{(2)}{\mathrm{R^1OCH_2CH_2O\dot{C}HR^2}} \tag{6}$$

$$\underset{(1)}{\mathrm{R^1OCH_2CH_2OCH_2R^2}} \xrightarrow{-\mathrm{H}} \underset{(3)}{\mathrm{R^1OCH_2\dot{C}HOCH_2R^2}} \text{ or } \underset{(4)}{\mathrm{R^1O\dot{C}HCH_2OCH_2R^2}} \tag{7}$$

$$\underset{(2)}{\mathrm{R^1OCH_2CH_2O\dot{C}HR^2}} \xrightarrow{\beta\text{ fission}} \underset{(5)}{\mathrm{R^1OCH_2CH_2\cdot}} + \underset{(6)}{\mathrm{OCHR^2}}\ (\mathrm{R^2 = H, CH_2OH,\ and\ CH_2OCH_3}) \tag{8}$$

$$\underset{(3)}{\mathrm{R^1OCH_2\dot{C}HOCH_2R^2}} \xrightarrow{\beta\text{ fission}} \underset{(7)}{\mathrm{R^1O\cdot}} + \underset{(8)}{[\mathrm{CH_2{=}CHOCH_2R^2}]} \tag{9}$$

$$\underset{(3)}{\mathrm{R^1OCH_2\dot{C}HOCH_2R^2}} \xrightarrow{\beta'\text{ fission}} \underset{(9)\ (\mathrm{R^1 = H\ and\ CH_3})}{\mathrm{R^1OCH_3CHO}} + \underset{(10)}{\mathrm{\cdot CH_2R^2}} \tag{10}$$

$$\underset{(5)}{\mathrm{R^1OCH_2CH_2\cdot}} \xrightarrow{-\mathrm{H}} \underset{(11)}{[\mathrm{R^1OCH{=}CH_2}]} \tag{11}$$

$$\underset{(5)}{\mathrm{R^1OCH_2CH_2\cdot}} \xrightarrow{\text{H abstraction}} \underset{(12)\ (\mathrm{R^1 = H})}{\mathrm{R^1OCH_2CH_3}} \tag{12}$$

$$\underset{(5)}{\mathrm{R^1OCH_2CH_2\cdot}} \xrightarrow{\cdot\mathrm{OH}} \underset{(13)\ (\mathrm{R^1 = H\ and\ CH_3})}{\mathrm{R^1OCH_2CH_2OH}} \tag{13}$$

$$\underset{(7)}{\mathrm{R^1O\cdot}} \xrightarrow{\text{H abstraction}} \underset{(14)\ (\mathrm{R^1 = H\ and\ CH_3})}{\mathrm{R^1OH}} \tag{14}$$

$$\underset{(7)}{\mathrm{R^1O\cdot}} \xrightarrow{-\mathrm{H}} \underset{(15)\ (\text{only with } \mathrm{R^1 = CH_3})}{\mathrm{HCHO}} \tag{15}$$

$$\underset{(10)}{\mathrm{\cdot CH_2R^2}} \xrightarrow{\text{H abstraction}} \underset{(16)\ (\mathrm{R = H\ and\ CH_2OH})}{\mathrm{CH_3R^2}} \tag{16}$$

$$\underset{(10)}{\mathrm{\cdot CH_2R^2}} \xrightarrow[-2\mathrm{H}]{\cdot\mathrm{OH}} \underset{(17)\ (\mathrm{R^2 = H, CH_2OH,\ and\ CH_2OCH_3})}{\mathrm{R^2CHO}} \tag{17}$$

$$\underset{(10)}{\mathrm{\cdot CH_2R^2}} \xrightarrow{(10)} \underset{(18)\ (\mathrm{R^2 = H})}{\mathrm{R^2CH_2CH_2R^2}} \tag{18}$$

Radicals (4a, c, and d) (R^1 = H in these cases) may undergo base-catalysed reaction [equation (20)], giving R^2CH_2OH and CH_3CHO, which may also be formed by β fission [equations (22)—(24)]. Radicals (4a, c, and d) also give alkoxyaldehyde (25) to small extent [equation (26)].

Formation of acetic acid is favoured *via* equations (20) and (21) than *via* equations (22)—(25), because the photolysis of EME in aqueous H_2O_2 gives little acetic acid at pH *ca.* 7, where base catalysis is impossible. The yield of acetic acid increases by displacement of the terminal methoxy- by a hydroxy-group, *i.e.*, EDE

$$\underset{(15)}{\mathrm{HCHO}} \xrightarrow{\mathrm{O}} \underset{(19)}{\mathrm{HCOOH}} \tag{19}$$

$$\underset{(4\mathrm{a,\ c,\ and\ d})}{\mathrm{HO\dot{C}HCH_2OCH_2R^2}} \xrightarrow[-\mathrm{H_2O}]{\mathrm{OH^-}} \underset{(20)}{\mathrm{{}^-O\dot{C}HCH_2OCH_2R^2}} \xrightarrow{\beta\text{ fission}} \mathrm{\cdot CH_2CHO} + \mathrm{{}^-OCH_2R^2}\ [\textit{i.e.}\ \mathrm{HOCH_2R^2}\ (21)] \tag{20}$$[15]

$$\mathrm{\cdot CH_2CHO} \xrightarrow{\text{H abstraction}} \underset{(22)}{\mathrm{CH_3CHO}} \xrightarrow{\mathrm{O}} \underset{(23)}{\mathrm{CH_3COOH}} \tag{21}$$[16]

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[13] R. J. Cvetanovic, *Adv. Photochem.*, 1963, **1**, 115.

[14] A. F. Trotman-Dickenson, *Adv. Free Radical Chem.*, 1967, **2**, 2.

[15] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1974, 824.

[16] J. Castonguay and Y. Rousseau, *Canad. J. Chem.*, 1971, **49**, 2125.

(3.6%) < EME (9.7%); DEDE (trace) < DEME (18.2%) < DEG (62.4%). This shows that radicals bearing a methoxy-group ionise in alkaline media to

$$\underset{(4a,\ c,\ and\ d)}{HO\dot{C}HCH_2OCH_2R^2} \xrightarrow{\beta\ fission} HOCH{=}CH_2 + \underset{(24)}{\cdot OCH_2R^2} \qquad (22)$$

$$HOCH{=}CH_2 \xrightarrow{rearrangement} \underset{(22)}{CH_3CHO} \xrightarrow{O} \underset{(23)}{CH_3COOH} \qquad (23)$$

give β-fission products [equation (20)], but radicals bearing a CH_2OCH_3 group are cleaved by equation (9) instead of (20). Radical (20) in equation (20) produces acetic acid *via* acetaldehyde. The alternative process [(22)—(25)] yields acetic acid much less efficiently with all these starting materials.

$$\underset{(24)}{R^2CH_2O\cdot} \begin{cases} \xrightarrow{H\ abstraction} \underset{(21)\ (R^2\,=\,H,\ CH_2OH,\ and\ CH_2OCH_3)}{R^2CH_2OH} & (24) \\ & or \\ \xrightarrow{-H} \underset{(17)\ (R^2\,=\,H,\ CH_2OH,\ and\ CH_2OCH_3)}{R^2CHO} & (25) \end{cases}$$

Vinyl ethers (8) and (11) especially methyl vinyl ether are known to polymerise easily to water-soluble polymeric products.[17] The material balance of carbon (total yield of carbon-containing products) decreases by substitution of the terminal hydroxy-group of glycol by methoxy, *i.e.*, EG (95.7%) > EME (45.3%) > EDE (43.3%); DEG (93.7%) > DEME (54.8%) > DEDE (35.7%). This decrease may be ascribed to the polymerisation of intermediate vinyl ethers to a tar which cannot be characterised. According to equation (9), methoxyl radical is formed in an amount equivalent to methyl vinyl ether (8) from EDE; thus the yield of methanol may approximate to that of methyl vinyl ether, since the yields of HCHO and HCOOH, the other products from $CH_3O\cdot$, are small [equations (14) and (15)]. But actually methyl vinyl ether suffers oxidative degradation, hence this expectation could not be proved. The corrected total recovery of carbon is almost 100% *with* EDE and with other substrates 105 for EDE, 92 for EME, 87—97 for DEDE, and 103% for DEME. Little hydrolysis of vinyl ethers (8) and (11) to acetaldehyde (*e.g.*, $CH_3OCH{=}CH_2 \longrightarrow CH_3CHO + CH_3OH$) was observed under our alkaline conditions. The expected oxidation products from vinyl ethers, CH_3OH, R^1CH_2OH, HCHO, HCOOH, and CO_2, were formed in small amounts in spite of the electron-rich nature of the vinyl ethers. Hence this also supports the fact that vinyl ethers were preferentially consumed by polymerisation.

$$\underset{(27)}{CH_3OCH_2CH_2OCH_2OH} \begin{cases} \xrightarrow{H_2O} \underset{(13b)\ (EME)}{CH_3OCH_2CH_2OH} + HCHO & (29) \\ \xrightarrow{-2H} \underset{(28)}{CH_3OCH_2CH_2OOCH} & (30) \end{cases}$$

Two main products from EG, HCHO, and HCOOH suggest that oxidation of EG proceeds mainly *via* C–C fission. In contrast to the case of EME, DEME, and DEG, little acetic acid was produced. Hence, base-catalysed dehydration of radical (26), formed by hydrogen-atom abstraction from EG [equation (27)] does not occur. Therefore, equations (20) and (21) could not be applied to the case of EG. EG is oxidised directly to form HCHO and HCOOH, where four or more mol. equiv. of the oxidant are required for EG. Hence, the conversion of EG is smaller than those of EDE and other substrates. It is of interest to note that the photo-oxidation of EG gives ethanol. Since photodecomposition of neat EG to ethanol is negligible,[18]

$$\underset{(24a,\ c,\ and\ d)}{HO\dot{C}HCH_2OCH_2R^2} \xrightarrow{-H} \underset{(25)\ (R^2\,=\,H)}{OHCCH_2OCH_2R^2} \qquad (26)$$

$$HOCH_2CH_2OH \xrightarrow{-H} \underset{(26)}{HO\dot{C}HCH_2OH} \qquad (27)$$

$$\underset{(1b)}{CH_3OCH_2CH_2OCH_3} \xrightarrow{O} \underset{(2b)}{CH_3OCH_2CH_2OCH_2\cdot} + \cdot OH(or\ ClO^-) \longrightarrow \underset{(27)}{CH_3OCH_2CH_2OCH_2OH} \qquad (28)$$

some kind of reduction must occur even under these highly oxidative conditions.

Among photoproducts from EDE, a compound (molecular weight 106) was obtained, probably $CH_3OCH_2CH_2OCH_2OH$ (27). The fragment pattern of (27) in mass spectra shows fragment ion ($M - 17$) but no dehydrated fragment ion ($M - 18$), because the lack of β-hydrogen inhibits dehydration, expelling only $\cdot OH$ [*i.e.*, (27) $\longrightarrow CH_3OCH_2CH_2OCH_2{\vdots}OH$]. The structure (27) is supported also by the formation of formate $CH_3OCH_2CH_2OOCH$ (28). The alternative structure, $CH_3OCH_2CH(OH)OCH_3$, is less probable because neither $CH_3OCH_2CO_2CH_3$ nor $CH_3OCH_2CO_2H$ was detected. The formation of (27) implies the insertion of atomic oxygen to the primary C–H bond. It is well known

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[17] Kirk–Othmer Encyclopedia, ' Chemical Technology ', Wiley-Interscience, New York, 1968, 2nd edn., vol. 17, pp. 391—410.

[18] V. der Linde, *Photochem. Photobiol.*, 1971, **13**, 147.

that (27) is easily hydrolysed in alkaline media to HCHO and EME. Insertion reaction may proceed *via* hydrogen atom abstraction by atomic oxygen followed by coupling of two resulting radicals.[19] Compound (27) may also be formed by the further oxidation of (2b) by some other oxidising agents such as ClO^-. Other substrates, EME, DEDE, and DEME, undergo analogous reactions to give EG, DEME, and DEG, respectively.

Only a trace of chlorinated product ($CHCl_3$) was obtained which seems to be a product of the halogenoform reaction of NaOCl with intermediate products such as ethanol and acetaldehyde. But in thermal reaction of EDE with aqueous NaOCl, the formation of chlorinated products is more appreciable, which is accounted for by the preference of halogenoform reaction at higher temperature.

EXPERIMENTAL

Materials.—Aqueous sodium hypochlorite was prepared by bubbling Cl_2 into ice-cooled aqueous NaOH in the dark, the precipitate of NaCl being filtered off. The solution can be stored for several weeks in a refrigerator. The concentration of hypochlorite was determined by iodometry before use.

All organic materials, EG, b.p. 197—198°, EME, b.p. 123—124°, EDE, b.p. 82—83°, DEG, b.p. 244—245°, DEME, b.p. 192—193°, DEDE, b.p. 160—161°, were first grade commercial materials, and used after distillation. No impurities were detected by g.l.c. in these materials.

Photo-oxidation.—Irradiation was carried out using a 300 W high-pressure mercury lamp in a cylindrical 8 × 200 mm quartz vessel. An aqueous solution of 0.9M-substrate (25 ml) was added with aqueous 0.45M-NaOCl (50 ml) and then diluted with water to 100 ml. This solution (*ca.* 40 ml) was introduced into a quartz cell, and irradiated at *ca.* 17°. The solution was kept ice-cooled before and after irradiation to prevent the thermal reaction.

Analysis.—Analysis of organic products was mainly done by g.l.c. using a Yanagimoto GCG 180 gas chromatograph equipped with flame ionisation and thermal conductivity detectors Two columns, PEG 20M (1.0 m) and Porapak QS (1.0 m), were used. Irradiated solution (2—5 μl) was injected onto the g.l.c. columns. The products were identified by comparison of g.l.c. peaks with those of authentic samples for two columns, and the estimation of yield was done by g.l.c. using internal standards such as 2-ethoxyethanol and propan-2-ol.

The products, after being condensed by evaporation, were also identified by g.l.c.–m.s. with a Schimadsu GCMS-7000 mass spectrometer employing a 1.5 m copper column packed with Porapak QS. The main *m/e* values are listed in Table 3. Formaldehyde was estimated by colorimetry (chromotropic acid method [20]).

The gaseous products evolved during the reaction were collected in a gas burette, and then analysed by g.l.c. using a 1.5 m copper column packed with Porapak type T after absorption of CO_2 by aqueous $Ba(OH)_2$ and O_2 by pyrogallol solution.

Carbon dioxide was absorbed in Na_2CO_3 in an alkaline reaction solution. The solution was then acidified with H_2SO_4, and CO_2 was expelled from the mixture by a flow of nitrogen, absorbed by aqueous 0.1N-$Ba(OH)_2$, and then estimated by titration with 0.1N-HCl.

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