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Photo-induced Oxidation of Diethylene Glycol Dimethyl Ether and Analogues with Aqueous Hydrogen Peroxide[1a)]

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Photo-oxidation of diethylene glycol dimethyl ether(DEDE), ethylene glycol dimethyl ether(EDE) and ethylene glycol monomethyl ether(EME) in the presence of aqueous H_2O_2 has been studied. DEDE and EDE give photo-oxidation products containing methanol, EME, methoxyacetaldehyde, methoxyacetic acid and methyl formate. EME gives products containing methanol, methoxyacetaldehyde and methyl formate. The oxidation is started by hydrogen atom abstraction by HO· radicals formed by the photolysis of H_2O_2. A reaction mechanism leading to the products(derived by initial C–O and C–C fissions) is postulated.

The photolysis of ethylene glycol monomethyl ether (EME) alone gives formaldehyde, methane, methanol, hydrogen *etc.*,[1b)] while that of EME and ethylene glycol dimethyl ether(EDE) under oxygen atmosphere gives formaldehyde, methanol, methyl formate.[2)]

However, no data are available on the photo-oxidation of glycols and their ethers in the presence of hydrogen peroxide. We are interested in this photo-oxidation as a model reaction for the photo-oxidative removal of nonionic surfactants in waste water which are difficult to remove biologically.

Here we wish to present data on the products and probable schemes for the photo-oxidation of diethylene glycol dimethyl ether(DEDE), EDE and EME in the presence of aqueous H_2O_2. Most of the experiments were carried out with DEDE, since it is the most suitable model compound for polyethylene glycols.

Results

A. Diethylene Glycol Dimethyl Ether(DEDE). *Products*: The photo-oxidation products of 0.25 M DEDE in the presence of 0.48 M H_2O_2 in water at pH 3.9 in a quartz tube with a high-pressure Hg lamp for 1 h gave the following products after vacuum distillation: CH_4, C_2H_6, CH_3OH, CH_3CHO, HCO_2CH_3, HCO_2H, $HOCH_2CH_2OH$, CH_3OCH_2CHO, $CH_3OCH_2CH_2OH$-(EME), $CH_3OCH_2CO_2H$, $HCO_2CH_2CH_2O_2CH$ and $CH_3OCH_2CH_2OCH_2CH_2OH$. The products were identified by GC-MS analysis and also by GLC analysis in comparison with GLC peaks of authentic samples using two kinds of columns.

Photolysis of H_2O_2. The rate of photo-oxidation of 0.184 M DEDE with 0.937 M H_2O_2 in water at pH 3.7 was measured at 20 °C by iodometry of H_2O_2 and GLC analysis of substrate (Table 1A). With the progress of reaction, the yields of the products changed (Table 1B).

$$\text{Yield (\%)} = \frac{\text{[produced product] (M)}}{\text{[decomposed substrate] (M)}} \times \frac{\text{carbon number of product}}{\text{carbon number of substrate}} \times 100$$

The decomposition of H_2O_2 is of zeroth-order within 60 min, and over two equivalents of H_2O_2 are necessary in order to decompose DEDE(Table 1A).

The yields changed only in a small range after 20 min irradiation(Table 1B). This suggests fast attainment of steady state in which the formation and consumption of the intermediates are fairly balanced.

TABLE 1A. PHOTO-DECOMPOSITION OF 0.937 M H_2O_2 AND 0.184 M DEDE IN AQUEOUS SOLUTION AT 20 °C

Irrad. time min	[H_2O_2] M	Dec [H_2O_2] %	[DEDE] M	Dec [DEDE] %
0	0.937	—	0.184	—
10	0.888	5.2	0.168	8.7
20	0.833	11.1	0.141	23.4
30	0.766	18.2	0.103	44.0
40	0.700	25.3	0.072	61.0
60	0.598	36.2	0.060	67.2

TABLE 1B. YIELDS OF PRODUCTS WITH THE PROGRESS OF PHOTOLYSIS OF DEDE–H_2O_2 AT 20 °C

Irrad. time min	CH_3OH %	HCO_2H %	HCO_2CH_3 %	CH_3OCH_2CHO %	$CH_3OCH_2CH_2OH$ (EME) %	$CH_3OCH_2CO_2H$ %
10	15.8	—	3.4	8.4	39.1	8.6
20	10.5	—	3.0	6.0	18.8	4.4
30	8.1	—	1.6	4.6	17.9	3.0
40	5.6	trace	1.9	5.1	17.1	2.6
60	10.2	1.0	1.6	5.3	16.9	2.0

TABLE 2A. EFFECT OF INITIAL CONCENTRATION OF H_2O_2 ON PHOTO-OXIDATION OF DEDE[a]

Run	$[H_2O_2]_0$ M	Dec $[H_2O_2]$ M	$[DEDE]_0$ M	Dec [DEDE] M	Dec [DEDE] %
1	2.85	0.239	0.194	0.114	58.8
2	1.90	0.359	0.191	0.129	67.7
3	0.927	0.391	0.200	0.146	73.2
4	0.208	0.174	0.186	0.086	46.0
5	0.095	0.085	0.183	0.048	26.0

a) Irradiated for 1 h in H_2O at 20 °C.

TABLE 2B. EFFECT OF INITIAL CONCENTRATION OF H_2O_2 ON THE PRODUCTS YIELDS IN PHOTO-OXIDATION OF DEDE[a]

Run	$[H_2O_2]_0$ M	CH_3OH %	HCO_2H %	HCO_2CH_3 %	CH_3OCH_2CHO %	$CH_3OCH_2CH_2OH$ (EME) %	$CH_3OCH_2CO_2H$ %
1	2.85	7.2	0.8	4.8	1.1	10.2	3.6
2	1.90	7.9	1.6	3.4	3.1	11.4	2.8
3	0.927	7.2	0.8	1.6	3.8	12.5	1.5
4	0.208	8.1	trace	trace	6.3	17.7	0.9
5	0.095	7.9	—	trace	6.6	20.7	0.9

a) Irradiated for 1 h in H_2O at 20 °C.

Effect of Initial Concentration of H_2O_2. In order to examine the contribution of H_2O_2 to the oxidation of DEDE, the effects of initial concentration of H_2O_2 ($[H_2O_2]_0$) on the oxidation rate of DEDE(Table 2A) and on product distribution(Table 2B) were studied with a nearly constant initial concentration of DEDE.

The decomposition of DEDE is proportional to that of H_2O_2, indicating the efficient oxidation of the substrate by H_2O_2. The decomposition rates of H_2O_2 in runs 1—3(Table 2A) are greater than those in runs 4 and 5. The number of absorbed photon per unit time is almost constant regardless of the initial concentration of H_2O_2 and substrate. Thus the observed variation of decomposition rates of H_2O_2 with change of $[H_2O_2]_0$ indicates the presence of a scheme for the decomposition of H_2O_2 induced by HO· radicals and/or other radicals generated by substrate decomposition. The product distribution depends considerably on $[H_2O_2]_0$. The yields of methoxyacetic acid, methyl formate and formic acid increase with increasing $[H_2O_2]_0$. The effect of $[H_2O_2]_0$ on the yields of methoxyacetaldehyde and ethylene glycol monomethyl ether (EME) is reversed, these products being more susceptible to further oxidation as compared with other products.

Effect of Pyrex-filtered Light. Photo-oxidation with light through a Pyrex-filter was examined with an aqueous mixture of 0.060 M DEDE and 1.18 M H_2O_2 at pH 3.6 for 5 h. The conversion of substrate was 28% after 1 h; 39% after 2 h; 47% after 3 h; 63% after 5 h. Photo-oxidation in a Pyrex vessel is slower than that in a quartz vessel, since Pyrex absorbs 250 nm light which is much more effective for decomposition of H_2O_2 than above 300 nm light.

Formation of CO_2. To test the possibility of complete oxidation of DEDE, an aqueous mixture of

TABLE 3. YIELDS OF PRODUCTS IN PHOTO-OXIDATION OF 0.223 M EDE WITH 0.909 M H_2O_2 AT 20 °C

Irrad. time min	Dec $[H_2O_2]$ %	Dec [EDE] %	CH_3OH %	HCO_2CH_3 %	CH_3OCH_2CHO %	EME %	$CH_3OCH_2CO_2H$ %
5	2.8	11.2	19.4	8.5	trace	25.8	2.9
10	7.4	24.3	15.7	6.9	2.5	22.9	3.1
15	11.6	35.8	14.5	7.8	2.1	19.6	2.0
20	16.5	42.3	14.6	7.3	3.7	16.2	1.8
30	27.3	57.1	14.3	6.0	4.1	16.2	1.3

TABLE 4. YIELDS OF PRODUDTS IN PHOTO-OXIDATION OF 0.167 M EME WITH 0.919 M H_2O_2 AT 20 °C

Irrad. time min	Dec $[H_2O_2]$ %	Dec [EME] %	CH_3OH %	HCO_2H %	HCO_2CH_3 %	CH_3CO_2H %	CH_3OCH_2CHO %
5	2.9	5.4	30.2	—	trace	—	11.8
10	4.6	13.6	18.8	trace	3.1	—	8.0
15	7.3	13.8	24.5	0.1	4.5	trace	9.2
20	7.8	20.6	19.5	0.1	3.2	0.1	8.0
30	13.8	40.1	16.1	0.2	2.4	0.2	6.6

0.0711 M DEDE and 1.16 M H_2O_2 was irradiated for 29 h. The CO_2 gas evolved, which was absorbed in aqueous $Ba(OH)_2$, was 77.5% of calculated value from the substrate. Taking into account the probable loss of CO_2, polyglycols may be completely converted to CO_2 and water after long irradiation.

B. Ethylene Glycol Dimethyl Ether (EDE). Photo-oxidation of 0.233 M EDE with 0.909 M H_2O_2 in water at pH 3.7 afforded the same products as those from DEDE, but with different composition (Table 3).

C. Ethylene Glycol Monomethyl Ether (EME). Photo-oxidation of 0.167 M EME with 0.919 M H_2O_2 in water gave the same products as those from EDE along with acetic acid (Table 4).

Discussion

The absorption coefficients(ε) for H_2O_2 and DEDE in an aqueous solution were measured at 250 nm, which is the principal wavelength of the high-pressure Hg lamp employed. The values of ε were: 26.4(250 nm) for H_2O_2, 0.437(250 nm) for DEDE, 0.94(300 nm) for H_2O_2, 0.36(315 nm) for H_2O_2 and 0(over 300 nm) for DEDE. Thus the photolysis of DEDE itself should be negligible in comparison with that of H_2O_2. The same is true with other substrates(EDE and EME). The initial step for the photo-oxidation should be the excitation and photo-decomposition of H_2O_2 as[3,4]

$$H_2O_2 \xrightarrow{h\nu} [H_2O_2]^* \longrightarrow 2\cdot OH. \qquad (1)$$

The hydroxyl radicals formed are known to react, abstracting H-atom from both substrate and another molecule of H_2O_2.[4,5]

$$HO\cdot + H_2O_2 \longrightarrow H_2O + HOO\cdot \qquad (2)$$

The HOO· radicals may abstract H-atom from substrate and add to substrate radicals. Otherwise, HOO·radicals disappear by reacting with each other ($2\,HOO\cdot \rightarrow H_2O_2 + O_2$) or with H_2O_2 ($HOO\cdot + H_2O_2 \rightarrow H_2O + O_2 + \cdot OH$).[4,5]

The products observed from DEDE can be explained by the following:

$$\underset{\mathbf{1}\ \text{(DEDE)}}{CH_3OCH_2CH_2OCH_2CH_2OCH_3} \xrightarrow[-H_2O]{\cdot OH}$$

$$\longrightarrow \underset{\mathbf{2}}{\dot{C}H_2OCH_2CH_2OCH_2CH_2OCH_3} \qquad (3)$$

$$\longrightarrow \underset{\mathbf{3}}{CH_3O\dot{C}HCH_2OCH_2CH_2OCH_3} \qquad (4)$$

$$\longrightarrow \underset{\mathbf{4}}{CH_3OCH_2\dot{C}HOCH_2CH_2OCH_3} \qquad (5)$$

The H-atom may be abstracted from 3-positions of DEDE as shown by Eqs. 3, 4, and 5. Their rates of abstraction were calculated to be *ca.* $3.6\times10^8\ M^{-1}\,s^{-1}$ for Eq. 3 and $5.6\times10^8\ M^{-1}\,s^{-1}$ for Eqs. 4 and 5 on the basis of the reported abstraction rates for CH_3OH ($0.6\times10^8\ M^{-1}\,s^{-1}$) and RCH_2OR ($1.4\times10^8\ M^{-1}\,s^{-1}$).[6]

Three radicals (**2**, **3**, and **4**) formed from DEDE by H-atom abstraction may undergo β-fission and/or HOO·radical addition to give products and/or other radicals(Eqs. 6—15). The products and radicals produced by Eqs. 6—15 may undergo secondary reaction to give fairly stable products (Eqs. 16—38), all of which were identified.

$$\underset{\mathbf{2}}{\cdot CH_2OCH_2CH_2OCH_2CH_2OCH_3} \xrightarrow{\beta\text{-fis.}} HCHO + \underset{\mathbf{5}}{\cdot CH_2CH_2OCH_2CH_2OCH_3} \qquad (6)^{8a,8b)}$$

$$\xrightarrow{HO\cdot\ (\text{or } H_2O_2)} \underset{\mathbf{6}}{HOCH_2OCH_2CH_2OCH_2CH_2OCH_3} \qquad (7)$$

$$\underset{\mathbf{3}}{CH_3O\dot{C}HCH_2OCH_2CH_2OCH_3} \xrightarrow{\beta\text{-fis.}} \underset{\mathbf{7}}{CH_3\cdot} + \underset{\mathbf{8}}{OHCCH_2OCH_2CH_2OCH_3} \qquad (8)$$

$$\xrightarrow{\beta\text{-fis.}} \underset{\mathbf{9}}{CH_3OCH{=}CH_2} + \underset{\mathbf{10}}{\cdot OCH_2CH_2OCH_3} \qquad (9)$$

$$\xrightarrow{HOO\cdot} \underset{\mathbf{11}}{CH_3OCH(OOH)CH_2OCH_2CH_2OCH_3} \qquad (10)^{2)}$$

$$\xrightarrow{H^+} \underset{\mathbf{12}}{CH_3\overset{+}{O}{=}CH\text{-}CH_2\cdot} + \underset{\text{(EME)}}{HOCH_2CH_2OCH_3} \qquad (11)^{7,8a)}$$

$$\underset{\mathbf{4}}{CH_3OCH_2\dot{C}HOCH_2CH_2OCH_3} \xrightarrow{\beta\text{-fis.}} \underset{\mathbf{13}}{CH_3O\cdot} + \underset{\mathbf{14}}{CH_2{=}CHOCH_2CH_2OCH_3} \qquad (12)$$

$$\xrightarrow{\beta\text{-fis.}} CH_3OCH_2CHO + \underset{\mathbf{15}}{\cdot CH_2CH_2OCH_3} \qquad (13)$$

$$\xrightarrow{HOO\cdot} \underset{\mathbf{16}}{CH_3OCH_2CH(OOH)OCH_2CH_2OCH_3} \qquad (14)^{2)}$$

$$\xrightarrow{H^+} CH_3OH + \underset{\mathbf{17}}{\cdot CH_2\text{-}CH{=}\overset{+}{O}CH_2CH_2OCH_3} \qquad (15)^{7,8a)}$$

$$\underset{\mathbf{5}}{\cdot CH_2CH_2OCH_2CH_2OCH_3} \xrightarrow{HO\cdot\ (\text{or } H_2O_2)} \underset{\text{(DEME)}}{HOCH_2CH_2OCH_2CH_2OCH_3} \qquad (16)^{8a,8b)}$$

$$\underset{\mathbf{6}}{HOCH_2OCH_2CH_2OCH_2CH_2OCH_3} \xrightarrow[\text{solvolysis}]{H_2O} HCHO + \underset{\text{(DEME)}}{HOCH_2CH_2OCH_2CH_2OCH_3} \qquad (17)$$

$$\underset{\mathbf{7}}{CH_3\cdot} \left|\begin{array}{ll} \xrightarrow{\text{H-abstr.}} CH_4 & (18) \\ \xrightarrow{CH_3\cdot} C_2H_6 & (19) \end{array}\right.$$

$$\underset{\mathbf{9}}{CH_2{=}CHOCH_3} \left|\begin{array}{ll} \xrightarrow[\text{solvolysis}]{H_2O} CH_3CHO + CH_3OH & (20)^{9)} \\ \xrightarrow{HO\cdot} \underset{\mathbf{18}}{CH_3O\dot{C}HCH_2OH} & (21)^{10)} \end{array}\right.$$

$$\underset{\mathbf{10}}{\cdot OCH_2CH_2OCH_3} \left|\begin{array}{ll} \xrightarrow{\text{H-abstr.}} \underset{\text{(EME)}}{HOCH_2CH_2OCH_3} & (22) \\ \xrightarrow{HO\cdot\ (\text{or } H_2O_2)} OHCCH_2OCH_3 + H_2O & (23)^{8a,8b)} \end{array}\right.$$

$$\underset{\mathbf{11}}{CH_3OCH(OOH)CH_2OCH_2CH_2OCH_3} \longrightarrow HCO_2CH_3 + \underset{\mathbf{19}}{HOCH_2OCH_2CH_2OCH_3} \qquad (24)^{2)}$$

$$\underset{\mathbf{12}}{CH_3\overset{+}{O}{=}CHCH_2\cdot} \left|\begin{array}{ll} \xrightarrow{H_2O} CH_3OH + CH_3CHO & (25) \\ \xrightarrow{H_2O,\,HO\cdot,\,-H^+} \underset{\mathbf{20}}{CH_3OCH_2OH} + HCHO & (26)^{7)} \end{array}\right.$$

$$\underset{\mathbf{13}}{CH_3O\cdot} \left|\begin{array}{ll} \xrightarrow{\text{H-abstr.}} CH_3OH & (27) \\ \xrightarrow[\text{disprop.}]{CH_3O\cdot} HCHO + CH_3OH & (28)^{11)} \end{array}\right.$$

$$\underset{\mathbf{14}}{CH_2{=}CHOCH_2CH_2OCH_3} \left|\begin{array}{ll} \xrightarrow[\text{solvolysis}]{H_2O} CH_3CHO + \underset{\text{(EME)}}{HOCH_2CH_2OCH_3} & (29)^{9)} \\ \xrightarrow{HO\cdot} \underset{\mathbf{21}}{HOCH_2\dot{C}HOCH_2CH_2OCH_3} & (30)^{10)} \end{array}\right.$$

$$\underset{\mathbf{15}}{CH_2CH_2OCH_3} \xrightarrow{HO\cdot\ (\text{or } H_2O_2)} \underset{\text{(EME)}}{HOCH_2CH_2OCH_3} \qquad (31)$$

$$\underset{\mathbf{16}}{CH_3OCH_2CH(OOH)OCH_2CH_2OCH_3} \longrightarrow \underset{\mathbf{20}}{CH_3OCH_2OH} + \underset{\mathbf{22}}{HCO_2CH_2CH_2OCH_3} \qquad (32)^{2)}$$

$$\underset{\mathbf{17}}{\cdot CH_2CH{=}\overset{+}{O}CH_2CH_2OCH_3} \left|\begin{array}{ll} \xrightarrow{H_2O} CH_3CHO + \underset{\text{(EME)}}{HOCH_2CH_2OCH_3} & (33) \\ \xrightarrow{H_2O,\ HO\cdot,\ -H^+} \underset{\mathbf{19}}{HOCH_2OCH_2CH_2OCH_3} + HCHO & (34) \end{array}\right.$$

$$\underset{\mathbf{18}}{CH_3O\dot{C}HCH_2OH} \xrightarrow{H^+} \underset{\mathbf{12}}{CH_3\overset{+}{O}{=}CHCH_2\cdot} + H_2O \qquad (35)^{7,8a)}$$

$$\underset{\mathbf{19}}{HOCH_2OCH_2CH_2OCH_3} \xrightarrow[\text{solvolysis}]{H_2O} HCHO + \underset{\text{(EME)}}{HOCH_2CH_2OCH_3} \qquad (36)$$

$$\underset{\mathbf{20}}{CH_3OCH_2OH} \xrightarrow[\text{solvolysis}]{H_2O} HCHO + CH_3OH \qquad (37)$$

$$\underset{\mathbf{21}}{CH_3OCH_2CH_2O\dot{C}HCH_2OH} \xrightarrow{H^+} \underset{\mathbf{17}}{CH_3OCH_2CH_2\overset{+}{O}{=}CHCH_2\cdot} + H_2O \qquad (38)^{7,8a)}$$

Table 5. GC-MS analysis of photolysis of DEDE

Compound	M^+	*m/e* (main value)									
CH_3OH	32	32	31	30	29						
CH_3CHO	44	44	43	31	29						
HCO_2H	46	46	45	44	29	28	18				
HCO_2CH_3	60	60	44	32	31	29	15				
$HOCH_2CH_2OH$	62	62	61	46	45	44	33	31	29	15	
CH_3OCH_2CHO	(74)[a]	73	60	46	45	44	43	31	29	15	
$CH_3OCH_2CH_2OH$	76	76	58	47	46	45	44	43	31	29	15
$CH_3OCH_2CO_2H$	(90)[a]	74	60	58	45	43	33	31	29	15	
$HCO_2CH_2CH_2O_2CH$	(118)[a]	72	60	45	44	43	33	29			

a) No M^+ was detected.

Acid-catalyzed decomposition of radicals in Eqs. 11 and 15 were postulated for the oxidation of 1,2-diols with Ti(III) peroxide system in acidic media at lower pH (≤ 2).[7,8a] The acidity was in pH range 3.5—4.0. With the progress of oxidation the acidity increased gradually to pH$\approx$3. Therefore, the contribution of Eqs. 11 and 15 to the reaction of radicals would be less than that of the reaction with H_2O_2 in higher concentration. The observed increase of acidity may be due to the formation of acidic products.

The processes for the formation of alkyl radicals (Eqs. 6, 8, and 13) are less probable than those for the formation of alkoxyl radicals(Eqs. 9 and 12) because of the stability of alkoxyl radicals as compared with alkyl radicals.

The presence of peroxides such as **11** and **16** is suggested from the reported photochemical autoxidation of EDE and EME.[2] These peroxides afford C–C fission products, methyl formate and formadlehyde hemiacetal, respectively(Eqs. 24 and 32). Disproportionation of methoxyl radical to formaldehyde and methanol (Eq. 28) was reported.[11]

Equations 20 and 29 are those of well-known acid-catalyzed solvolysis of vinyl ethers.[9] The reactions between vinyl ethers and HO·radical (Eqs. 21 and 30) were studied by ESR spectroscopy.[10] Equations 36 and 37 are also those of well-known acid-catalyzed hydrolysis of hemiacetal.

The unexpectedly low yields of formic acid and formaldehyde are ascribed to their facile oxidation to CO_2 in the presence of H_2O_2. Only trace of products **8** and **22** was detected by GC-MS and GLC analyses.

In the photo-oxidation of EME, the yield of MeOH is larger than that of methoxyacetaldehyde, hence the C–O fission appears to occur preferentially at the ether linkage rather than at the hydroxyl linkage. As shown in Table 4, the conversion of EME and H_2O_2 is generally low. Thus further oxidation product (*e.g.*, methoxyacetic acid) from methoxyacetaldehyde is smaller than that shown in Tables 2B and 3.

The formation of acetic acid in photo-oxidation of EME may be due to the preferential C–O fission of **23** at the ether linkage (Eq. 39) and/or due to acid-catalyzed reaction of **18** (Eqs. 35 and 26) and **23** (Eq. 41). The acetaldehyde formed should undergo the further oxidation by H_2O_2 or O_2 (Eq. 42).

$$CH_3OCH_2\dot{C}HOH \quad \mathbf{23}$$

$$\xrightarrow{\beta\text{-fis.}} CH_3O\cdot + CH_2{=}CHOH(\text{or } CH_3CHO) \qquad (39)$$

$$\xrightarrow{HO\cdot \text{ or } H_2O_2} CH_3OCH_2CHO \qquad (40)$$

$$\xrightarrow{H^+} CH_3OH + \cdot CH_2CH{=}\overset{+}{O}H \qquad (41)^{7,8a)}$$

$$CH_3CHO \xrightarrow{O} CH_3CO_2H \qquad (42)$$

Experimental

Materials. Commercial diethylene glycol dimethyl ether(DEDE), bp 160—161 °C, ethylene glycol dimethyl ether(EDE), bp 82—83 °C and ethylene glycol monomethyl ether(EME), bp 123—124 °C of first grade materials were used after distillation. Their GLC analyses showed single peaks. Hydrogen peroxide (90%, Mitsubishi Gas Chem. Co.) was used.

Photo-oxidation. An ice-cooled aqueous solution of DEDE was mixed with ice-cooled 90% H_2O_2 with stirring. The mixture was introduced into a quartz cell and warmed to room temperature. The cell was irradiated at 20 °C with a 300 W high-pressure Hg lamp through a water filter or a Pyrex filter. After completion of reaction, the mixture was cooled with ice.

Analyses. The ice-cooled mixture was analyzed by iodometry in order to determine the content of H_2O_2. The organic products were analyzed by GLC. After being condensed by evaporation, the products were analyzed by GC-MS. GLC analysis was carried out with a Yanagimoto GCG 550F gas chromatograph with a hydrogen flame ionization detector employing two kinds of columns, Porapak QS and PEG 20M. The products were identified by comparison of GLC peaks with those of authentic samples in two columns. Estimation of yield was carried out by GLC with a Porapak QS using 2-propanol as an internal standard.

The GC-MS analysis of the products was carried out with a Shimadzu GCMS-7000 mass spectrometer with a column of Porapak QS. The main *m/e* values of products are given in Table 5.

The CO_2 evolved was absorbed in saturated aqueous $Ba(OH)_2$ and titrated with HCl. The organic gaseous products were collected in a gas burette and analyzed by GLC (TCD and FID) using columns of Porapak QS and Porapak T. The acidity was measured with a Hitachi-Horiba M-7 type pH meter.

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