Reactions of 1,1-Dialkoxyalkene Radical Cations in Aqueous Solution with OH^-, HPO_4^{2-}, and H_2O. Electron Spin Resonance Spectroscopic, Pulse Conductometric, and Product Analytical Studies

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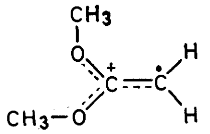
The reactions of H_2O, HPO_4^{2-}, and OH^- with eight 1,1-dialkoxyalkene radical cations have been studied in aqueous solution by e.s.r. spectroscopy and in part by pulse conductometry and product analysis. Hydroxide ion reacts with the radical cations with rate constants ranging from k 2 × 10^8 for species (5) to 6 × 10^9 l mol^{-1} s^{-1} for (6), producing mainly alkoxycarbonylalkyl radicals. With (1) and with (6), in addition, the formation of 1,1-dialkoxy-2-hydroxyethyl radicals was observed and e.s.r. parameters are given. The HPO_4^{2-} anion was found to react with four of the radical cations to form phosphato-dianion-substituted radicals, $(RO)_2(PO_4^{2-})C-\dot{C}H_2$ (e.s.r. parameters are given), with k values ranging from 2 × 10^6 for (1) to 3 × 10^8 l mol^{-1} s^{-1} for (6). Water reacted analogously with rate constants ranging from k 3 × 10^2 for (1) to 10^4 s^{-1} for (27) at 20 °C, the reaction yielding 2,2-dialkoxy-2-hydroxyethyl radicals (e.s.r. parameters are given) and protons. Attack of water occurs virtually only at the dioxygen-substituted carbon as is shown in one example. Product analysis by g.l.c.–m.s. of the higher boiling material from ^{60}Co γ-irradiation of N_2O-saturated aqueous solutions of $(CH_3O)_2CH-CH_2Cl$ gave evidence for the formation of dimers and cross-dimers of the radicals $\dot{C}H_2OCH(OCH_3)CH_2Cl$, $CH_3OCO\dot{C}H_2$, $(CH_3O)_2CH-\dot{C}HCl$, $(CH_3O)_2\dot{C}HCH_2$, and $(CH_3O)_2\dot{C}H_2OH$. Structures and yields of the products agree with the conclusions drawn from e.s.r. spectroscopic and conductometric measurements.

We have previously [1] described the formation, structure, and conformation of the 1,1-dialkoxyalkene radical cations (1)—(8) in aqueous solution. The open-chain species exist in the *Z,E*-conformation; (3) and (4) are stereoisomers. The radical cations were formed on heterolytic dissociation of 1,1-dialkoxyalkyl radicals, or cyclic analogues thereof, which possess leaving groups such as Br, Cl, or $OCOCH_3$ β to the radical site, *e.g.* (9) or (10) [see reaction (1)].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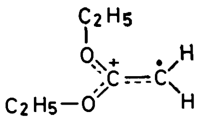
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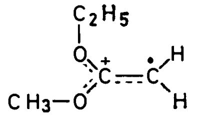
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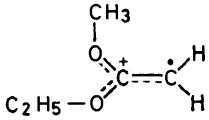
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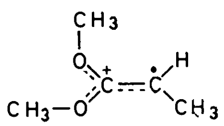
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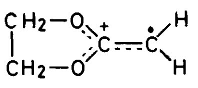
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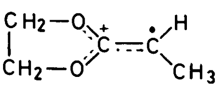
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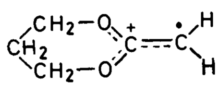
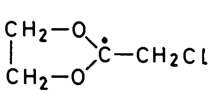

(8)

The precursor radicals, *e.g.* (9) or (10), were obtained among other radicals by hydrogen abstraction from the corresponding substrates by OH˙, $SO_4^{\cdot -}$, or triplet acetone. The radical cations could be observed in aqueous solution by room-temperature e.s.r. spectroscopy using *in situ* techniques with a photolytic flow system or time dependent conductometric measurements in combination with pulse radiolysis.

$(CH_3O)_2\dot{C}CH_2Cl$

(9)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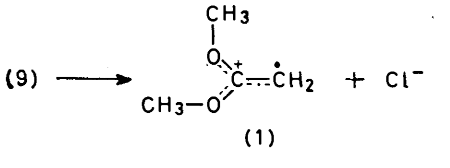

(1)

The electrophilic reactivity of the radical cations towards water was unexpectedly low, a fact that rendered their observation in aqueous solution possible. They were best observed in acidic solutions at pH ≤ 6. Under such conditions [with the exception of (6)] their decay followed second-order kinetics and this was assigned to the bimolecular reactions (2a or b). The resulting cations or dications react immediately with water [reactions (2c and d)], yielding dimers and protons. The rate constants for reaction (2a and b) approach the diffusion-controlled limit.[1] Radical cation (6) showed a first-order decay *versus* time to which reaction (3) was assigned (k_3 7 × 10^3 s^{-1}). Bimolecular decay of (6), analogous to reactions (2), may be expected at much higher dose rates, and, *vice versa*, pseudo-first-order decay of the other radical cations of this series, analogous

$$R^{\bullet+} + R^{\bullet+} \longrightarrow {}^{+}R{-}R^{+} \qquad (2a)$$

$$R^{\bullet+} + R^{\bullet}_{x} \longrightarrow {}^{+}R{-}R_{x} \qquad (2b)$$

$$R^{\bullet+} = \text{radical cation}; \; R^{\bullet}_{x} = \text{other radical}$$

$${}^{+}R{-}R^{+} + 2\,H_2O \longrightarrow \text{products} + 2H^{+} \qquad (2c)$$

$${}^{+}R{-}R_{x} + H_2O \longrightarrow \text{products} + H^{+} \qquad (2d)$$

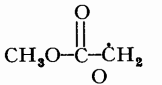
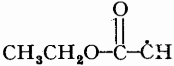
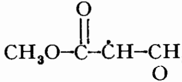
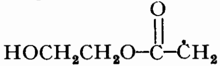
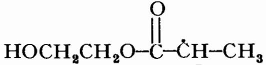
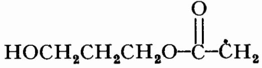
$$(6) + \text{water} \longrightarrow \text{radicals (s)} + H^{+} \qquad (3)$$

to reaction (3), may prevail at much lower dose rates, and hence at lower radical concentrations, than used in pulse radiolysis, *e.g.* under ^{60}Co γ-irradiation where the dose rates used in this laboratory are *ca.* 100—10 000 times lower.

It was briefly mentioned previously [1] that the radical cations (1)—(8) undergo fast reactions with OH^-. In the present paper a more detailed account of the electrophilic reactivity of the radical cations is given. In particular, the kinetics of the addition reactions with OH^-, HPO_4^{2-}, and H_2O is presented and the structure of the resulting radicals is described. In selected cases characteristic products were analysed and their *G* values determined. The regioselectivity of nucleophilic attack by H_2O was explored in the case of a chlorine-containing radical cation. In one case a complete product analysis of the final dimeric products was carried out.

TABLE 1

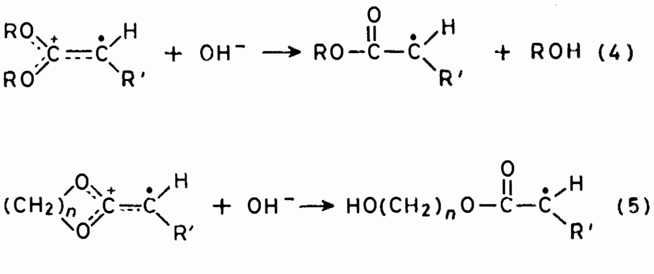
E.s.r. parameters and pH ranges of formation of alkoxycarbonylalkyl radicals from 1,1-dialkoxyalkene radical cations in aqueous solutions at 3 °C; pH limits between 4 and 10 refer to phosphate buffered solutions. Experimental conditions: u.v. irradiation of aqueous solutions containing 0.3M-acetone, 0.02M-$K_2S_2O_8$, 0.05M-Na_2HPO_4, and 0.04—0.2M-β-halogeno- or β-acetoxy-substituted acetals or cyclic acetals (see text and ref. 1) in a flow system.

Radical cation(s)	Radical		pH range	Hyperfine splittings (mT) number of protons in parentheses			
				a_{α}^{H}	a_{β}^{H}	a_{δ}^{H}	*g* factor
(1), (3), (4)	 $CH_3O{-}C(=O){-}\dot{C}H_2$	(11)	≤1.5 and 8—12	2.135(2)		0.156(3)	2.003 34
(2)—(4)	 $CH_3CH_2O{-}C(=O){-}\dot{C}H_2$	(12)	5—11	2.140(2)		0.165(2)	2.003 32
(5)	 $CH_3O{-}C(=O){-}\dot{C}H{-}CH_3$	(13)	9—12	2.03(1)	2.49*(3)	0.165(3)	2.0033*
(6)	 $HOCH_2CH_2O{-}C(=O){-}\dot{C}H_2$	(14)	≤2.5 and 4.5—12	2.142(2)		0.160(2)	2.003 34
(7)	 $HOCH_2CH_2O{-}C(=O){-}\dot{C}H{-}CH_3$	(15)	8—11	2.02*(1)	2.47*(3)	0.17*(2)	2.0033*
(8)	 $HOCH_2CH_2CH_2O{-}C(=O){-}\dot{C}H_2$	(16)	≤2.5 and 6—12	2.140(2)		0.166(2)	2.003 34

* Low accuracy due to low signal : noise ratio or to multiple line overlap.

RESULTS AND DISCUSSION

(a) *Reactions with* OH^-.—The methods used in generating the radical cations (1)—(8) in alkaline solution lead to the formation of the alkoxycarbonylalkyl radicals (11)—(16) which were identified by e.s.r. spectroscopy from their *g* factors and splitting patterns (Table 1, Figures 1 and 2). The radicals (11), (13), and (14) have already been described.[2-4] It is assumed that the alkoxycarbonylalkyl radicals are formed by reactions of OH^- with the radical cations with elimination of alcohol [reaction (4)] or ring opening [reaction (5)]. The alcohols formed according to reaction (4) have been quantitatively analysed after ^{60}Co γ-irradiation of N_2O saturated aqueous solutions. Their yields expressed in terms of *G* values (100 eV yields) agree with *G*(halide) from the same substrates (Table 2). *G*(halide) is representative for the *G*-value of formation of the corresponding radical cation [*cf.* reaction (1)]. From the 1-ethoxy-1-methoxyethylene radical cations (3) and (4) both methanol and ethanol were obtained.



R = CH_3, C_2H_5; R' = H, CH_3; *n* = 2,3

In two cases the entry of OH^- at the terminal position of the radical cations was observed. Upon generating the radical cation (6) in alkaline solution, the 2-hydroxymethyl-1,3-dioxolan-2-yl radical (17) was detected in addition to (14). The new spectrum arises at pH ≥ 8.5 with low intensity (see Figure 2b). It comprises a

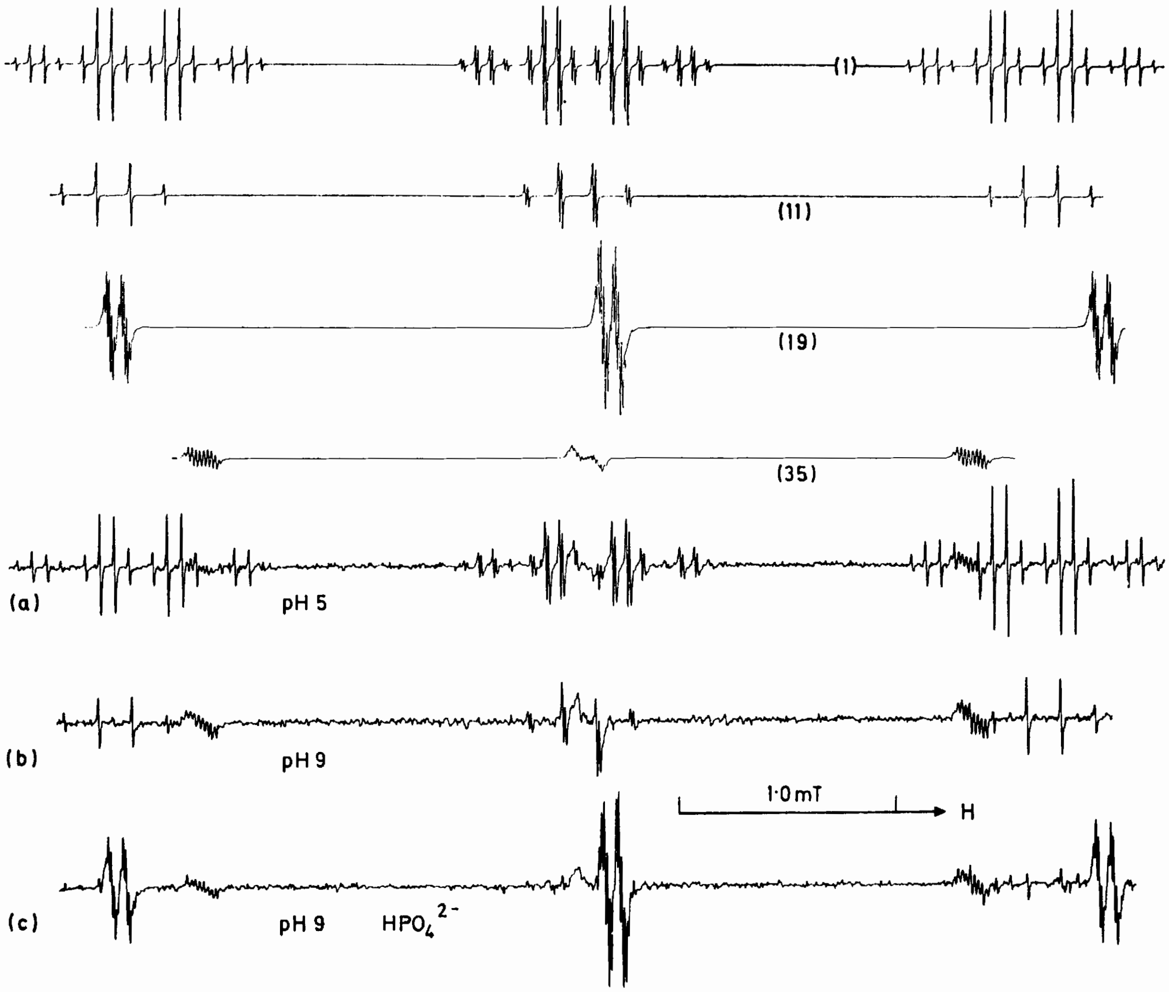
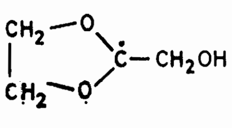


FIGURE 1 E.s.r. spectra obtained by u.v. irradiation of aqueous solutions of 0.3M-acetone, 0.02M-$K_2S_2O_8$, and 0.2M-2-chloro-1,1-dimethoxyethane at 3 °C in a flow system (a) at pH 5 (b) at pH 9 and 0.1M-borate buffer, (c) at pH 9 and 0.2M-Na_2HPO_4. The prominent spectrum of (a) arises from the *Z,E*-1,1-dimethoxyethylene radical cation (1). The spectrum of the [2-chloro-1-methoxyethoxy]methyl radical (35) is also recognizable. The spectrum of (b) arises from the methoxycarbonylmethyl radical (11) and from (35) and of (c) from the 2-phosphato-2,2-dimethoxyethyl radical dianion (19), from radical (35) and from a small contribution of radical (11). Simulated spectra of the species are given at the top of the Figure

triplet (from the two β-protons of the CH_2OH group), a small doublet (from the hydroxy-proton), and a quintet (from the four ring protons). The triplet exhibits selective broadening of the outer (m_I ± 1) lines with line heights in the ratio *ca.* 0.4 : 2 : 0.4 (rather than the expected 1 : 2 : 1). The radical appears to be pyramidal and in a conformation with the OH group eclipsed to the unpaired electron, as concluded from the equivalence of the β-protons, the small size of its splittings, and the line broadening. The form of the broadening (the central lines being unaffected) is explained by pyramidal inversions of the radical centre * at the 'locked' conformation of the CH_2OH group, leading to structures (A) and (B). Since structure (A) is expected to have smaller β-splittings than (B), the broadening of the outer lines can be understood in terms of the in-phase modulation of the β-splittings, assuming the rate of inversion to be 'intermediate'. The e.s.r. parameters are in accord with those of the related radical 2-methyl-1,3-dioxolan-

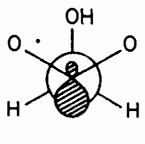


(17)

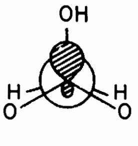
a^{H}_{β} 0.330(2) a^{OH}_{β} 0.018

a^{H}_{γ} 0.145(4) mT, g 2.00318

a^{OH}_{β} 0 at pH 12.6



(A)



(B)

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* This type of broadening is not expected for restricted rotation of the CH_2OH group at a planar radical centre; a broadening of the central lines is expected in this case.

2-yl [$a_{\gamma'}^{H}$ 0.120(4), a_{β}^{H} 1.285 (3) mT (for rotating CH_3 group), g 2.003 2, at 0 °C),[5] for which restricted rotation of the methyl group was found at low temperatures and which is assumed to be pyramidal. INDO Calculations for the locked conformation akin to (A) gave 0.322, 0.338, and 3.244 mT for the β-splittings.[5] The first two values support the assignment of the 0.330 mT triplet to the β-couplings of radical (17), which seem to be unusually small.

Apparently radical (17) is formed by addition of OH^- at the terminal position of the radical cation (6) according to reaction (6). It is assumed that this reaction is

$$(6) + OH^- \longrightarrow (17) \qquad (6)$$

slower than reaction (5) because the observed concentration of (17) was smaller than the one of (14). From the spectra the concentration of (17) was estimated as *ca.* 15—20% of that of radical (14) at pH 9.5—12, using solutions immediately after the pH adjustment.

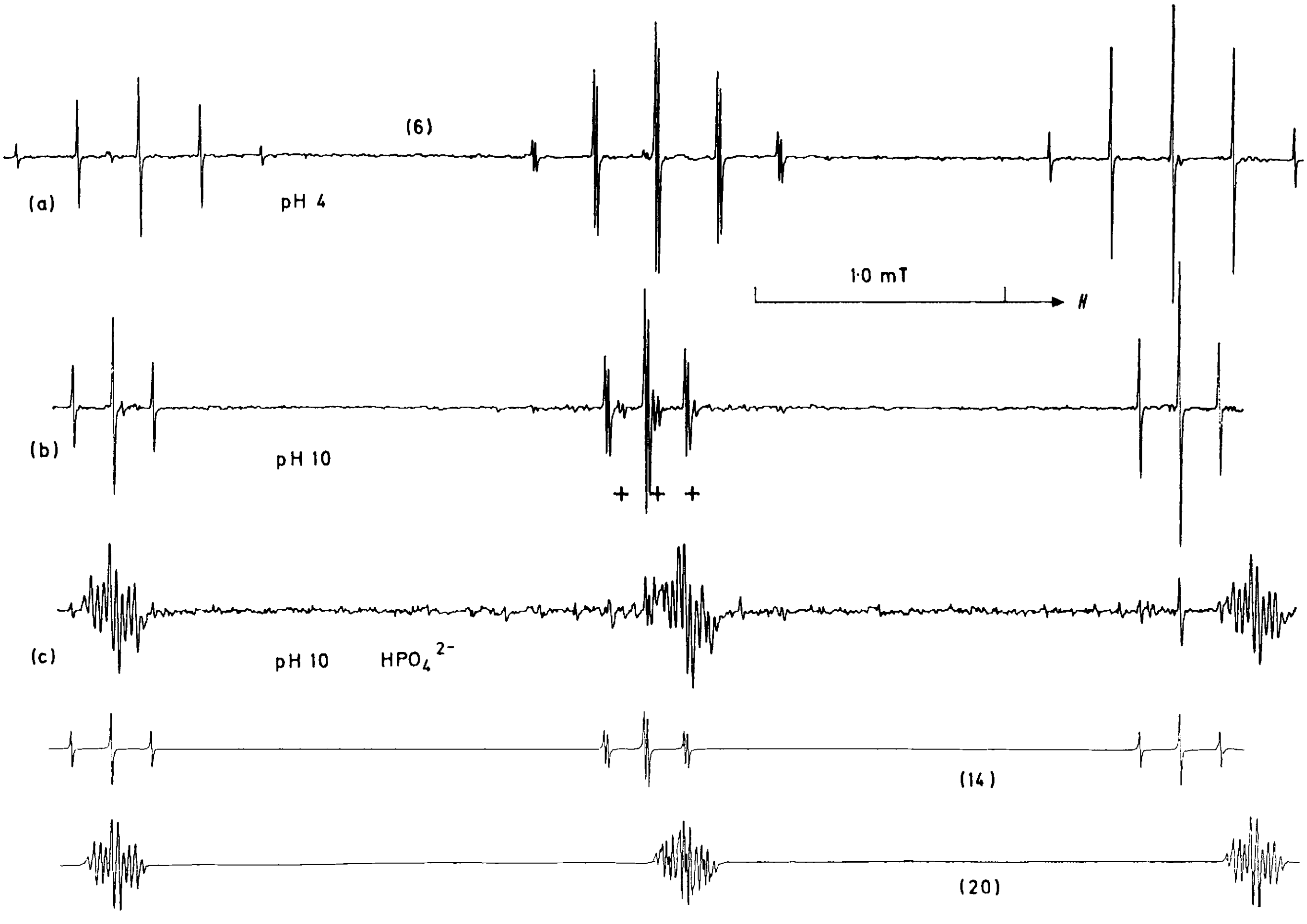
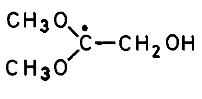


FIGURE 2 E.s.r. spectra of (a) the 2-methylene-1,3-dioxolan radical cation (6), (b) the 2-hydroxyethoxycarbonylmethyl radical (14), and the 2-hydroxymethyl-1,3-dioxolan-2-yl radical (17) [only lines of the central quintet are depicted +; the outer quintets are not seen due to line broadening, see text], (c) the (2-phosphato-1,3-dioxolan-2-yl)methyl radical dianion (20) and small amounts of radical (14), twofold sensitivity compared with (a) and (b). The simulated spectra of (14) and (20) are below (c). Experimental conditions: photolytic flow system at 3 °C, aqueous solutions of 0.3M-acetone, 0.02M-$K_2S_2O_8$, and 0.04M-2-chloromethyl-1,3-dioxolan, (a) at pH 4, (b) at pH 10 and 0.1M-$H_2BO_3^-$, and (c) at pH 10 and 0.2M-HPO_4^{2-}

With 2-chloro-1,1-dimethoxyethane as substrate besides radical (11) the radical 2,2-dimethoxy-1-hydroxyethyl (18) was observed at pH 9—12. The spectrum of



$(CH_3O)_2\dot{C}-CH_2OH$

(18)

a_{β}^{H} 0·592 (2), $a_{\beta}^{OH} \approx 0$

$a_{\gamma'}^{H}$ 0·073 (6) mT, g 2·0030

(18) shows selective broadening of the outer ($m_I \pm 1$) lines of the β-triplet pattern with line heights in the ratio *ca.* 0.6 : 2 : 0.6. The radical (18) appears to be in a conformation with the β-OH group eclipsed to the unpaired electron with the radical centre being pyramidal, presumably less in extent compared with (17). The signals of (18) were very weak when using freshly distilled substrate (see Figure 1b), but were well observed with substrate that had been kept in well capped bottles for several weeks in a refrigerator. Therefore, we are not certain to what extent radical (18) arises from reaction of OH^- with the radical cation (1).

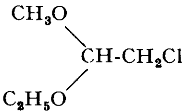
Besides the above radicals the acetate radical anion,

$\dot{\mathrm{C}}\mathrm{H_2COO^-}$, or the propionate radical anion, $\mathrm{CH_3\dot{C}HCOO^-}$, were also observed by e.s.r. spectroscopy, particularly so in strongly alkaline solutions. They are considered to be secondary products arising from the alkoxycarbonylalkyl radicals by $\mathrm{OH^-}$ catalysed hydrolysis.

The rate of $\mathrm{OH^-}$ attack at the radical cations was determined pulse conductometrically. The principles of this technique and a first example, $k_{[\mathrm{OH^-} + (1)]}$, were reported earlier.[1] The data are compiled in Table 3.

TABLE 2

G Values (100 eV yields) of low boiling products obtained from ^{60}Co γ-irradiated, N_2O-saturated aqueous solutions at 0° of 5×10^{-3}M solutions of selected acetals; error ±20% (see Experimental section). Dose rates, 1 400—1 600 Gy h^{-1} or 140—160 krad h^{-1}, doses applied causing 1—3% conversion of the acetals. *G* Values of HCl formation given previously [1] are included for comparison

Acetal	Radical cation	*G* Values of low boiling products	*G*(HCl)
$(\mathrm{CH_3O})_2\mathrm{CH{\cdot}CH_2Cl}$	(1)	$\mathrm{CH_3OH}$, 2.1; $\mathrm{CH_2O}$, 0.2; $\mathrm{CH_3COOCH_3}$, 0.5	2.5
	(3), (4)	$\mathrm{CH_3OH}$, 1.9; $\mathrm{C_2H_5OH}$, 0.7; $\mathrm{CH_3COOCH_3}$, 0.2; $\mathrm{CH_2O}$, 0.07; $\mathrm{CH_3CHO}$, 0.5	1.8
$(\mathrm{C_2H_5O})_2\mathrm{CH\text{-}CH_2Cl}$	(2)	$\mathrm{C_2H_5OH}$, 1.6; $\mathrm{CH_3CHO}$, 0.8; $\mathrm{CH_3COOC_2H_5}$, 0.2	1.5

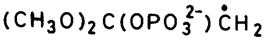
The largest value, $k_{[\mathrm{OH^-} + (6)]}$, is close to a diffusion-controlled limit whereas the smallest value of this series is *ca.* 30 times less. The size of the rate constants is markedly lower for the radical cations (5) and (7) compared with that for (1) and (6) (Table 3). The decreased reactivity of the former can be explained as a consequence of the electron-releasing capability of the methyl group attached to the radical site, which will increase the delocalization of the positive charge. This leads to decreased electrophilicity and thus to higher stability of the radical cations. On tracing the decay of the stereoisomers (3) and (4) e.s.r. spectroscopically no preferred disappearance of one of the two species could be observed.

(22), appeared instead (*see* Figures 1 and 2 and Table 4). The *g* factors, the a_α^{H} splittings and, where appropriate, the a_β^{H} splittings of the new radicals are typical of those observed with alkyl radicals. Small $a_{\delta'}^{\mathrm{H}}$ splittings and the appearance of the a^{P} doublet permit the assignment to phosphate-substituted radicals such as *e.g.* (19) or (21). Alternative structures for the observed radicals, *e.g.* $(\mathrm{CH_3O})_2\dot{\mathrm{C}}\text{-}\mathrm{CH_2\text{-}OPO_3^{2-}}$, were ruled out on the basis of the known spectrum of the radical [6] $\mathrm{CH_3O\text{-}\dot{C}H\text{-}CH_2\text{-}OPO_3^{2-}}$ (*g* 2.003 02, a_α^{H} 1.72, a_β^{H} 0.850, $a_{\gamma'}^{\mathrm{H}}$ 0.185, a^{P} 0.267 mT). The assignment of two negative charges to the phosphate group is based on the pH range of observation of radicals (19)—(22) and the assumption that the pK_a values are close to 7 as in alkyl phosphoric acids. Thus, the overall reaction for the formation of *e.g.* radical (22) can be written as in equation (7).

TABLE 3

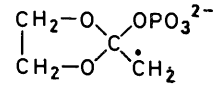
Rate constants of reactions of $\mathrm{OH^-}$ with selected 1,1-dialkoxyalkene radical cations in aqueous solution at 20 ± 2 °C in decreasing order as determined pulse conductometrically.[1] Error ±20%

Radical cation	$k_{(\mathrm{OH^-} + \mathrm{R^{\cdot+}})}$/l mol^{-1} s^{-1}
(6)	6.4×10^9
(1)	4.2×10^9
(3) + (4)	3.0×10^9
(2)	2.5×10^9
(27)	1.2×10^9
(8)	9.0×10^8
(7)	7.0×10^8
(5)	2.3×10^8

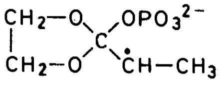


$(\mathrm{CH_3O})_2\mathrm{C}(\mathrm{OPO_3^{2-}})\dot{\mathrm{C}}\mathrm{H_2}$

(19)



(20)



(21)

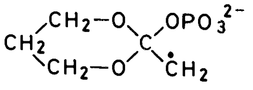


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TABLE 4

E.s.r. parameters of phosphato-dianion substituted radicals obtained from 1,1-dialkoxyalkene radical cations in aqueous solutions at 3 °C. Experimental conditions as given in Table 1, but with 0.1—0.2M-$\mathrm{HPO_4^{2-}}$

Radical cation	Radical	pH range	Hyperfine splittings (mT), number of protons in parentheses				
			a_α^{H}	a_β^{H}	$a_{\delta'}^{\mathrm{H}}$	a^{P}	*g* factor
(1)	(19)	8—12	2.270(2)		0.012(6)	0.068	2.002 41
(6)	(20)	8—12	2.275(2)		0.070(2) 0.025(2)	0.025 *	2.002 42
(7)	(21)	10—12	2.24 (1)	2.58(3)	0.035 *(4) †	0.06	2.002 4 *
(8)	(22)	9—12	2.29 (2)		0.025(2) 0.012(2)	0.075	2.002 41

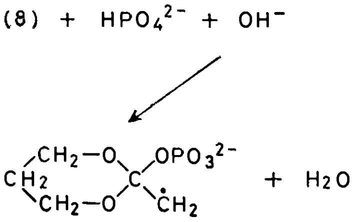
* Low accuracy due to low signal : noise ratio and multiple line overlap. † Mean value from non-equivalent protons.

(b) *Reactions with* $\mathrm{HPO_4^{2-}}$.—In alkaline solution and in the presence of $\mathrm{Na_2HPO_4}$ the formation of the alkoxycarbonylalkyl radicals from the radical cations (1) and (6)—(8) was in part suppressed and new radicals (19)—

From the observations reported above it follows that $\mathrm{OH^-}$ and $\mathrm{HPO_4^{2-}}$ compete for reaction with a radical cation. Therefore, the relative concentrations of the phosphate-substituted radicals on the one hand and of the alkoxycarbonylalkyl radicals, plus acetate or propionate radical, respectively, on the other hand depend on both the phosphate concentration and the pH, this being in accord with our e.s.r. spectroscopic observations. From the spectra pH values above 10 were taken at which the stationary concentrations of radicals obey equation (8).* Above pH 10 the radicals observed are formed irreversibly.* Assuming for simplicity equal rates of bimolecular termination for all radicals involved equation (9) is derived from which values for the ratio

$$k_{HPO_4^{2-}}[HPO_4^{2-}][R^{\cdot +}] = k_{OH^-}[OH^-][R^{\cdot +}] \qquad (9)$$

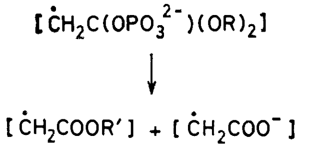
$k_{OH^-} : k_{HPO_4^{2-}}$ for the radical cations (1), (6), and (8) were obtained (see Table 5). The values represent the selectivities of the radical cations towards nucleophilic attack by OH^- and HPO_4^{2-}. With the radical cation (7) the e.s.r. spectra were too complicated to obtain data of this kind. Together with values for k_{OH^-} which were taken from Table 3 data for $k_{(HPO_4^{2-}} + R^{\cdot +}$, for the radical cations (1), (6), and (8) were calculated (see Table 5).



(7)

(22)

It is seen from Table 5 that the attack of HPO_4^{2-} on the radical cations is slower than that of OH^- and furthermore, that the sequence of electrophilic reactivity of the radical cations towards HPO_4^{2-} is (6) > (8) > (1). The sequence of reactivity towards OH^- was different, *viz.* (6) > (1) > (8); the reason for this behaviour is not yet clear.



(8)

R = alkyl, R′ = R or ROH

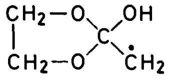
A decrease of the e.s.r. signals of the alkoxycarbonylalkyl radicals in the presence of HPO_4^{2-} was not observed with the radical cations (2)—(5) and no phosphate-substituted radicals were observed in these cases. One reason for this behaviour is seen in a further increase in the ratio $k_{OH^-} : k_{HPO_4^{2-}}$ for these radical cations as a consequence of their decreased electrophilicity compared with that of (1). A second is seen in the easier reversion of $\dot{R}OPO_3^{2-}$ radicals derived from (2)—(5) into their corresponding radical cations and phosphate (*cf.* ref. 6), which is another consequence of the lower electrophilicity of these radical cations towards phosphate. The lower electrophilicity of the radical cations (2)—(5) compared with (1) is already borne out in lower values of $k_{(OH^- + R^{\cdot +})}$ (*see* Table 3).

(c) *Reactions with* H_2O.—(i) *With the* 2-*methylene*-1,3-*dioxolan radical cation* (6). The radical cation (6) showed a pseudo-monomolecular decay in aqueous solutions at pH ⩽ 5 with k_3 7 × 10^3 s^{-1}. At 2 ⩽ pH ⩽ 4 besides (6) radical (23) was observed. At pH 2 the signals for (23) were rather weak and below pH 1.5 they were no longer observed while those of (6) were still of the same size. In the e.s.r. spectrum (23) appeared as a broad triplet which was clearly observed at higher microwave power levels (3—10 mW) (see Table 6).

TABLE 5

Values of $k_{4H^-}/k_{HPO_4^{2-}}$ (error ±20%) at 3 °C for the competitive attack of OH^- and HPO_4^{2-} on selected radical cations in aqueous solution from e.s.r. spectroscopy under the conditions of Table 4, using equation (9) (see text) and values for $k_{(HPO_4^{2-} + R^{\cdot +})}$ calculated therefrom using data for k_{OH^-} at *ca.* 20 °C from Table 3 for (6), and values corrected for 3 °C by a factor of 0.43 or 0.9 obtained from e.s.r. measurements of the decay of (1) or (8), respectively at 3 °C

Radical cation	$k_{OH^-}/k_{HPO_4^{2-}}$	$k_{(HPO_4^{2-} + R^{\cdot +})}$/l mol^{-1} s^{-1}
(6)	20	*ca.* 3 × 10^8
(8)	100	0.8 × 10^7
(1)	2 000	0.9 × 10^6



(23)

The assignment of the broad signals to (23) is based on the fact that the *g* factor and splittings are very similar to those of the structurally related phosphato-dianion substituted radical (20) (*see* Table 4). Radical (23) is then seen as the product of the addition of H_2O to the radical cation (6) according to reaction (10) (resulting in a pseudo-monomolecular kinetics).

$$(6) + H_2O \longrightarrow (23) + H^+ \qquad (10)$$

Radical (23) might also have been formed by attack of OH^- on (6); however, OH^- attack is calculated to be as fast as reaction (10) only at pH ⩾ 8 using the $k_{[OH^- + (6)]}$ value of Table 3. Therefore, at pH ⩽ 6 OH^- attack on (6) is negligible. From the decrease of [(23)] on reducing the pH to 2 and the fact that [(6)] increases *ca.* 40% (compared with pH 6) it is concluded that (23) decays into the parent radical cation (6) and water, according to reaction (11) which is the reverse of (10).

Radical (23) also decays into the 2-hydroxyethoxycarbonylalkyl radical (11) by acid catalysis according to reaction (12), as may be concluded from the appearance of (14) at pH ⩽ 2.5 (see Table 1). Below pH 2 the ratio

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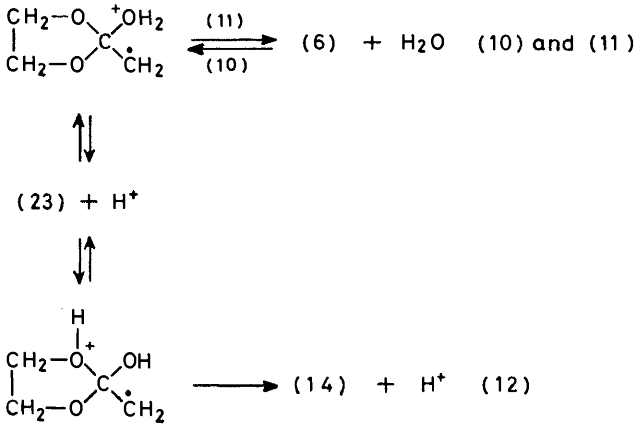
* The stationary concentrations of radicals were measured as a function of pH from 3 to 12 and with two phosphate concentrations. Further details will be presented elsewhere.

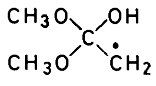
of the concentrations of (6) and (14) is pH independent in agreement with equations (10)—(12).* Radical (14) is known[4] to be reasonably stable in acidic solution. The reaction observed above pH 3.5 is (11) which must



(24)

therefore be faster than (12). The mechanism for the formation of (14) above pH 3.5 will be presented elsewhere.

(ii) *With other radical cations.* Broad e.s.r. signals similar to those of radical (23) were just detectable in addition to the spectra of the radical cations (1) and (8) in acidic solutions (*see* Table 6). Structures (25) and (26) are assigned to them. Since their pH range of observation is similar to that of (23) it is suggested that their mode of formation and decay is also analogous to that of (23) [reactions (13) and (14)]. Kinetic evidence for the occurrence of reactions (13a) and (14a) was obtained from pulse conductometric measurements (see Figure 3). In Figure 3 the reciprocal of the first half-life of the build-up of conductivity *versus* the dose rate is plotted for N_2O-saturated aqueous solutions of 2-chloro-1,1-dimethoxyethane, or 2-chloromethyl-1,3-dioxan, respectively. Under the conditions specified in the caption of Figure 3 the radical cations (1) or (8), respectively, are formed practically within the pulse duration of one microsecond. The subsequent build-up of



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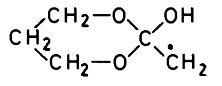

(26)

conductivity, determined after appropriate corrections (see ref. 1), is mainly of second order [see reactions (2)]. However, extrapolation to zero dose rate yields intersections with the ordinate which represent the reciprocal half-lives of the pseudo-first-order contribution to the conductivity, and are assigned to the decay of (1) or (8) according to reactions (13a) and (14a). It is assumed that under the conditions of Figure 3 the reverse reactions (13b) and (14b) do not significantly contribute to the measured rate constants. The rate constants for reactions (10), (13a), and (14a) are given in Table 7.

TABLE 6

E.s.r. parameters and pH range of observations of radicals resulting from the reaction of H_2O with selected radical cations in aqueous solution. Experimental conditions as given in Table 1, but in the absence of phosphate

Radical cation	Radical	pH range *	a^H_α/mT	linewidth (mT)	g factor †
(1)	(25)	2.5—4.5	2.285(2)	0.03	2.0024
(6)	(23)	2—4	2.285(2)	0.06	2.0024
(8)	(26)	2.5—4	2.28 †	0.07	2.0024

*Above pH 4 or 4.5 unbuffered solutions could no longer be used; phosphate as buffer was also effective as nucleophile, and in its presence the formation of radicals (23), (25), and (26) was suppressed. † Low accuracy due to multiple line overlap.

From the *k* values of Table 7 it follows that the sequence of electrophilic reactivity towards water is

$$(1) + H_2O \underset{b}{\overset{a}{\rightleftharpoons}} (25) + H^+$$

$$(25) + H^+ \xrightarrow{c} (11) + CH_3OH + H^+ \qquad (13)$$

$$(8) + H_2O \underset{b}{\overset{a}{\rightleftharpoons}} (26) + H^+$$

$$(26) + H^+ \xrightarrow{c} (16) + H^+ \qquad (14)$$

(6) > (8) > (1). This sequence is the same as towards phosphate and different from that towards OH^-. Attempts to discover radicals analogous in structure to (23), (25), or (26) with the other radical cations were in vain. For kinetic detection they probably react too slowly and for e.s.r. spectroscopic detection their

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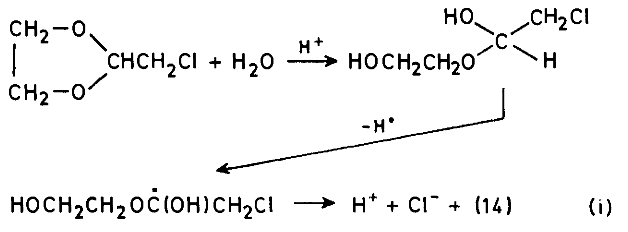
* Radical (14) was completely absent in the e.s.r. spectra at pH 3.5 independent of the approach to that pH value from pH 1.5 or 6. Therefore, an alternative route leading to radical (14)



consisting of acid-catalysed hydrolysis of the substrate followed by hydrogen abstraction and elimination of HCl according to reaction (i) is excluded.

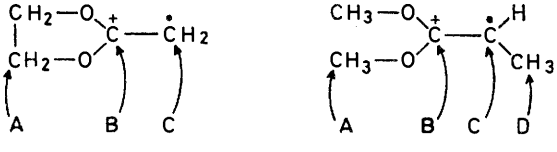
signals were very likely weak and buried among the many other lines.

(d) *The Regioselectivity of Nucleophilic Attack on the Radical Cations.*—In the radical cations several sites for the attack of nucleophiles must be considered (see Scheme 1). In analogous carbocations, in which the unpaired electron in the radical cations is replaced by hydrogen, nucleophilic attack is known to occur at site A or B in Scheme 1 depending on the structure of the cation, the nucleophile, and the reaction conditions.[7,8] Nucleophilic attack at site C should be favoured over attack at B for steric reasons. Nucleophilic attack at site D could conceivably lead to allyl radicals, a reaction which has its analogue in the deprotonation of aliphatic cations into olefins. However, nucleophilic attack at site D so far remains hypothetical: within the limits of e.s.r. spectroscopy there was no evidence for the formation of allyl radicals, according, *e.g.*, to reaction (15a), neither after attack of OH^-, nor HPO_4^{2-}, nor H_2O. An alternative route for deprotonation of the radical cation involves formation of a non-conjugated unsaturated radical [reaction (15b)]. But again, this type of radical was absent under all our conditions and deprotonation is apparently not fast enough to compete with the addition reactions observed.

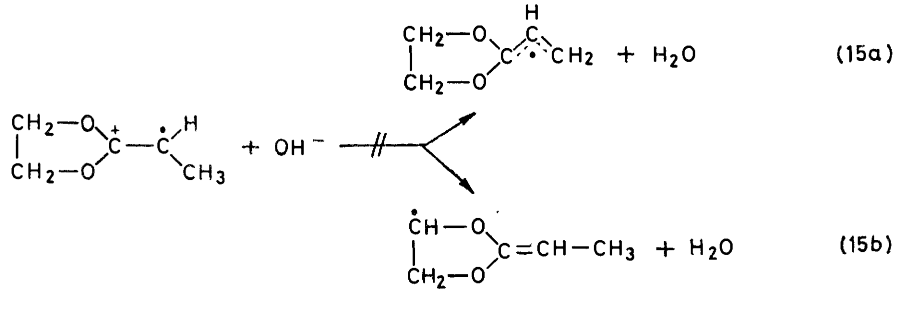
TABLE 7

Rate constants of reactions of selected radical cations with H_2O as determined pulse conductometrically (see text) at 20 ± 2 °C. Error ±20% for (6), (8), and (27), ±30% for (1)

Radical cation	$k_{(H_2O + R^{\bullet +})}/s^{-1}$
(27)	1.0×10^4
(6)	7.0×10^3
(8)	8.4×10^2
(1)	3.5×10^2



SCHEME 1



As for nucleophilic reactions of OH^-, HPO_4^{2-}, or H_2O the exclusion of the attack by H_2O at sites A and C is selected for presentation. The mechanism of reaction of OH^- and HPO_4^{2-} with the radical cations will be presented elsewhere. Nucleophilic attack of H_2O on site A of the radical cations is excluded due to the fact that in the range $2.5 < pH \leqslant 4$ the necessary products of such an attack, alkoxycarbonylalkyl radicals [reactions (16) or (17)], were not detected by e.s.r. spectroscopy although these radicals are easily observable. The radicals actually observed from the reactions of H_2O with (1), (6), and (8) at $pH \leqslant 4$ are (25), (23), or (26), respectively. These radicals could be formed either by addition of H_2O to site B of the radical cation followed by deprotonation of the adduct, *e.g.* according to reaction (18), or by attack at site C followed by isomerization of the adduct and subsequent deprotonation, *e.g.* according to reaction (19).

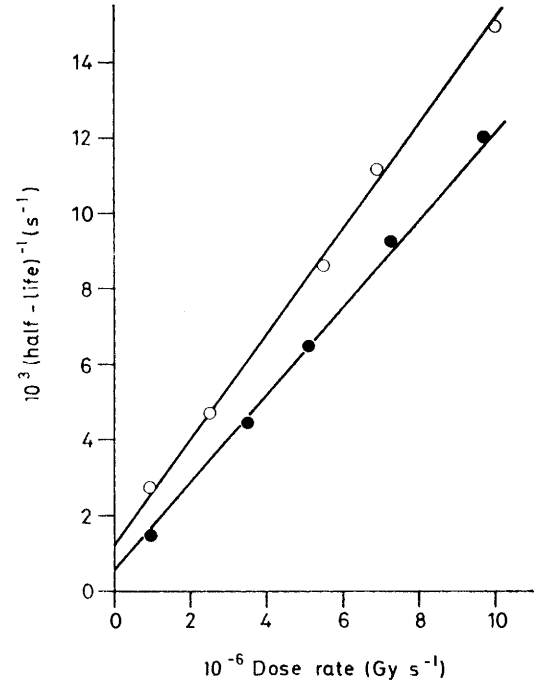


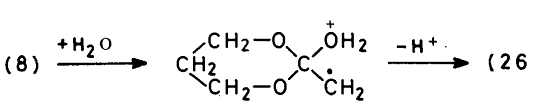
FIGURE 3 Plot of the reciprocal first half-life of the build-up of conductivity *versus* the dose rate after application of 10^{-6} s electron pulses of 2.8 MeV to N_2O-saturated aqueous solutions, at 20 ± 2 °C and pH 4.6, of 2×10^{-3}M-2-chloromethyl-1,3-dioxan, ○, of 2-chloro-1,1-dimethoxyethane, ●

Radical (17) was not observed from low pH to pH 8. This is possibly due to effective catalysis of the rearrangement of (17) to (23) by protons or by the buffer or the entry of water is more selective than the entry of

OH^- and occurs at the dioxygen-substituted carbon only. The latter is in accord with expectations from reactivity–selectivity considerations.

$$(1) + H_2O \not\longrightarrow CH_3OH + H^+ + (11) \qquad (16)$$

$$(6) + H_2O \not\longrightarrow (14) + H^+ \qquad (17)$$



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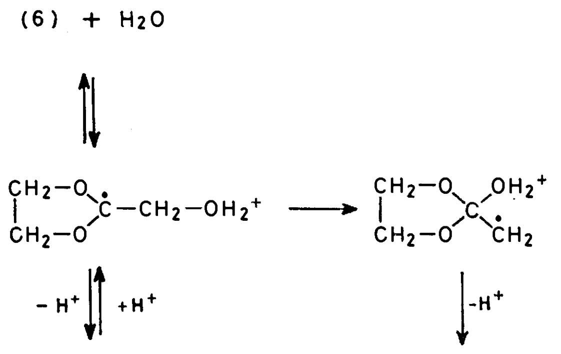
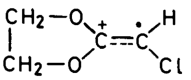


(17) (23) (19)

In order to exclude nucleophilic attack at site C in one example the 2-chloromethylene-1,3-dioxolan radical cation (27) was made by analogy with the other radical cations by hydrogen abstraction and Cl^- elimination from 2-dichloromethyl-1,3-dioxolan (28) in aqueous solution at pH $\leqslant 5$. Nucleophilic attack of H_2O at site B yields radical (29) and a proton according to reaction (20). Attack of H_2O at site C leads to radical (30) and a proton according to reaction (21). Whereas radical (29) is expected eventually to dimerize or cross-dimerize with other radicals without loss of Cl, radical (30) is expected to lose Cl by one of the following reactions: (a) by loss of H^+ and Cl^- and formation of radical (31), [reaction (22)], in less than a microsecond by analogy with reaction (1) or with rapid HCl elimination from the radical $Cl\dot{C}H-CHCl(OH)$ obtained by addition of OH radicals to 1,2-dichloroethylene in aqueous solution,[9] or (b) by isomerization of (30) into (32) according to reaction (23) followed by elimination of H^+ and Cl^- and formation of radical (31) according to reaction (24). [Isomerization of (30) into (29) appears to be very unlikely in view of the better migrating aptitude of Cl compared with OH.]



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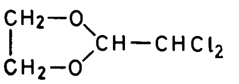
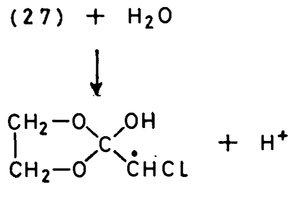


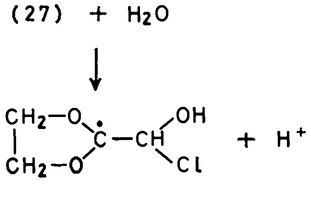
(28)

Reaction (24) has an analogy in the submicrosecond elimination of HCl from the radical $HO-\dot{C}H-CH_2Cl$ in aqueous solution.[10,11] One means of deciding on the matter would be to check whether the chlorine-containing radical (29) or the chlorine-free radical (31) was formed as an intermediate. E.s.r. spectroscopy in this case, however, gave broad lined complex spectra and no assignment could be made.

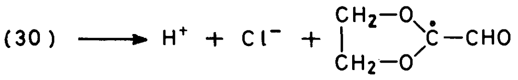
The *G* value for HCl formation was measured after ^{60}Co γ-irradiation of (28) (10^{-2}M) in N_2O-saturated aqueous solutions at 0 °C. The value, 3.6, was found to be independent of the dose rate which argues against contributions from chain reactions. In the case of nucleophilic attack of H_2O at site B, (29) is formed [reaction (20)] and with no further loss of Cl^- on bimolecular termination of (29) *G*(HCl) should equal *G*(27). However, nucleophilic attack of H_2O at site C, leads to the loss of the second Cl^-, and *G*(HCl) should by twice *G*(27). The measurement of the *G*(27) value is based on the *G*(HCl) value obtained after γ-irradiation of aqueous solutions of (28) which were saturated with a 4 : 1 N_2O–O_2, mixture. Under these conditions the



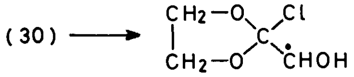
(29) (20)



(30) (21)

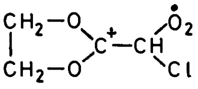


(31) (22)



(32) (23)

$$(32) \longrightarrow H^+ + Cl^- + (31) \qquad (24)$$



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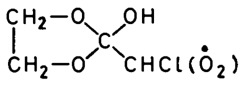
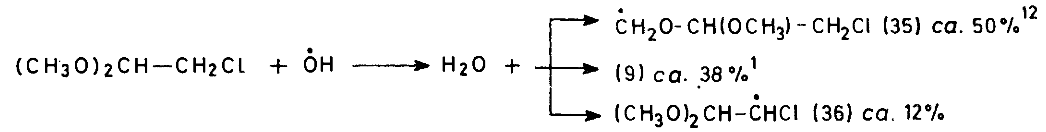


(34)

amount of hydrogen abstraction by OH radicals from (28) is unchanged [G(OH) 6.0] compared with O_2-free N_2O-saturated solutions, but hydrogen abstraction by hydrogen atoms [G(H) 0.6] no longer occurs because hydrogen atoms are scavenged by O_2 to form OOH radicals which do not abstract hydrogen from (28). In the presence of N_2O–O_2 the radical cation (27) is scavenged by O_2 and the peroxyl radical cation (33) is expected to be formed as a short-lived intermediate that quickly reacts with water to yield the radical (34) and a proton. Radical (34) is expected to eliminate HCl in subsequent reactions.* Therefore the G(HCl) value should equal $2G$(27). The G(HCl) value found was 6.1 (independent of dose rate which shows that chain reactions are absent). This result leads to $G(27) = 3.35$ taking in account the correction for G(H). A comparison of this value with that, G(HCl) 3.6, measured for O_2-free N_2O solutions (see above) shows that the main attack of H_2O occurs at site B, leaving only a small percentage of attack possible at site C.

(e) *Product Analysis after* ^{60}*Co* γ-*Irradiation*.—In order to obtain chemical support for the transformations which 1,1-dialkoxyalkene radical cations undergo in aqueous solution one case, the 1,1-dimethoxyethylene radical cation (1) was selected for closer study. For this purpose an N_2O-saturated aqueous solution of 10^{-2}M-2-chloro-1,1-dimethoxyethane, at 20 °C, was subjected to ^{60}Co γ-irradiation with a dose rate of *ca.* 1 400 Gy h^{-1}, the total dose applied causing *ca.* 30% conversion of the substrate. The remaining substrate and the products were obtained after neutralization with NaOH, extraction with ether, drying of the extract with Na_2SO_4, and evaporation of the solvent. The analysis of products with b.p. above that of the substrate was performed by g.l.c.–m.s. In the gas chromatogram of the higher boiling products there were three major peaks and four minor ones, from which mass spectra were taken, besides numerous very small peaks of trace components. In Table 8 the products have been arranged in the sequence of their peak sizes. The peak numbers refer to the sequence of elution. The analysis is only semi-quantitative, since, except for peak no. 1, no material for calibration was available.



SCHEME 2

TABLE 8

G.l.c.–m.s. analysis of products obtained after γ-irradiation of a N_2O-saturated aqueous solution of 10^{-2}-M-2-chloro-1,1-dimethoxyethane (see text). The g.l.c. peaks are numbered in their sequence of elution after the substrate peak. (For mass spectra and other details see Experimental section)

Peak no.	Quantity	Assignment	
5	Main product	$ClCH_2CH(OCH_3)OCH_2CH_2COOCH_3$	(35)—(11)
7	2nd major product	$ClCH_2CH(OCH_3)OCH_2CH_2OCH(OCH_3)CH_2Cl$	(35)—(35)
1	3rd major product	$CH_3OCOCH_2CH_2COOCH_3$	(11)—(11)
6	1st minor product, <5% of the total	$ClCH_2CH(OCH_3)OCH_2CH(Cl)CH(OCH_3)_2$	(35)—(36)
2	2nd minor product	$CH_3OCOCH_2CH(Cl)CH(OCH_3)_2$	(11)—(36)
3	3rd minor product	$ClCH_2CH(OCH_3)OCH_2CH_2CH(OCH_3)_2$	(35)—(37)
4	4th minor product, ~1—2% of the total	$ClCH_2CH(OCH_3)OCH_2C(OCH_3)_2CH_2OH$	(35)—(18)

The formation of the dimers is explained in the following way. The radicals formed by hydrogen-abstraction are (35), (9), and (36) (Scheme 2). Due to the incomplete scavenging of solvated electrons by N_2O a small percentage of the e^-_{aq} react with the substrate to yield radical (37) [reaction (25)]. Radical (9) undergoes fast conversion into the radical cation (1) [reaction (1)]. At the dose rate employed the mean radical lifetime with respect to diffusion-controlled bimolecular termination is of the order of 100 ms, ample time to

$$(CH_3O)_2CH\text{-}CH_2Cl + e^-_{aq} \longrightarrow \underset{(37)}{(CH_3O)_2CH\text{-}\dot{C}H_2} \qquad (25)$$

assure complete reaction of the radical cation (1) with water to yield radical (25), according to reaction (13a). Prior to or after dimerization of (25) the function $CH_2C(OH)(OCH_3)_2$ is converted into CH_2COOCH_3 and methanol (Table 2). Therefore, some of the products

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* Pulse conductometric measurements in the presence of N_2O–O_2 confirm the two-step formation of HCl: there was a rise in conductivity in the microsecond range and of first-order kinetics, assignable to reactions (ii) and (iii) and a conductivity change in

$$(27) + O_2 \longrightarrow (33) \qquad \text{(ii)}$$

$$(33) + H_2O \longrightarrow (34) + H^+ \qquad \text{(iii)}$$

the ms range, with second-order kinetics and of practically the same size as in the first step, which is assigned to reactions (iv) and (v). Thus there is also a kinetic differentiation of the

$$2\ (34) \longrightarrow \longrightarrow 2\ H^+ + 2\ Cl^- + \text{products} \qquad \text{(iv)}$$

$$(34) + R_x \longrightarrow \longrightarrow H^+ + Cl^- + \text{products} \qquad \text{(v)}$$

$$\dot{R}_x = \text{other radical}$$

elimination of the two Cl atoms in the presence of O_2. Details of the measurement and reactions of the radical cations with O_2 will be discussed elsewhere.

of Table 8 seem to be dimers or cross-dimers of the radical $CH_3OCO\dot{C}H_2$ (11), and this number has been used in the assignment of the monomeric structural unit in the corresponding dimers in Table 8. The formation of radical (25) and therefore of entity (11) is clear evidence for the occurrence of reaction (13a). The main product (Table 8) may be described as (35)—(11), the mixed dimer of radical (35) and entity (11). Next in quantity is (35)—(35), the dimer of the main radical followed in quantity by (11)—(11), the dimer of the second major entity, or its precursor, (25)—(25), respectively. Radical (36) which is the smallest in quantity among the hydrogen abstraction radicals appears in two minor products, (35)—(36) and (11)—(36), *viz.* as cross dimers with the major radicals (35) and (11). The dimer (36)—(36) was not among the products amounting to $>1\%$ of the total, which is in agreement with the low probability of dimerization of a minor component. Minor components may only be found in dimers with the main or the second main radical. Thus, two further minor radicals were scavenged by (35), *viz.* (37) and most likely (18). The assignment of peak no. 4 (Table 8) to the dimer (35)—(18), although in accord with the mass spectrum and the gas chromatographic retention sequence, needs further support and is at present only tentative. Note that radical (18) is observed by e.s.r. spectroscopy in alkaline solution though its genesis is uncertain. If peak no. 4 is correctly assigned this means that radical (18) is also relatively stable in acidic solution. Its formation through addition of H_2O to the sterically less hindered 2-position of (1) (followed by deprotonation) is as well conceivable as the analogous addition of OH^- to that position.

The structure of dimer (35)—(37) was confirmed by analysis of the products from γ-irradiation of an aqueous solution of $(CH_3O)_2CHCH_2Cl$ under argon instead of N_2O. Now (37) is produced as the main radical as well as (35) and the mixed dimer (35)—(37) was observed as a major product.

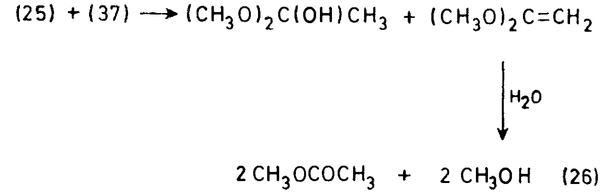
The structures of the dimers containing the ester function $-CH_2COOCH_3$, *viz.* (11)—(11), (11)—(35), and (11)—(36) were indirectly confirmed by a g.l.c. analysis of the products obtained after ^{60}Co γ-irradiation of an alkaline N_2O-saturated aqueous solution of $(CH_3O)_2CH-CH_2Cl$ and extraction with ether of the alkaline solution. The dimers containing the partial structure (11) were now missing while the others were still present. This is due to the saponification of the ester groups into methanol and a carboxylate group which renders the substances insoluble in ether. The structures of the remaining dimers are thereby confirmed in that they do not contain groups which suffer easy saponification.

While the mixed dimers (35)—(37) and (35)—(11) containing the main radical (35) were found the corresponding dimers containing the second major species (11) were apparently missing. This is probably because radicals (37) and (18) which have hydrogen atoms β to the unpaired electron undergo disproportionation by hydrogen transfer to (25) [reaction (26)] instead of cross-dimerization. A small amount of methyl acetate has actually been observed (Table 2).

The small amounts of formaldehyde obtained (Table 2) are assumed to be formed after disproportionation of radical (35) leading to $(\overset{\cdot\,+}{C}H_2O)(CH_3O)CHCH_2Cl$, then to $(HOCH_2O)(CH_3O)CHCH_2Cl$, and eventually to $CH_2O + CH_3OH + ClCH_2CHO$.

From the low G values for CH_2O and $CH_3O–CO–CH_3$ (Table 2) it is apparent that disproportionation of the radicals occurs only to a minor extent, dimerization being the main process in the bimolecular termination.

Summarizing, the structures of the dimers confirm the conclusions drawn from e.s.r. spectroscopy concerning



$$\begin{tikzcd}(25) + (37) \arrow[r] & (CH_3O)_2C(OH)CH_3 + (CH_3O)_2C{=}CH_2 \arrow[d, "H_2O"] \\ & 2\,CH_3OCOCH_3 + 2\,CH_3OH \quad (26)\end{tikzcd}$$

the transformation of the radical cations in aqueous solutions, especially the result that nucleophilic attack of H_2O on the 1,1-dimethoxyethylene radical cation (1) occurs to $>95\%$ at the 1-position and to $<5\%$ to the 2-position. This is in accord with INDO calculations for (1) [13] which indicate that the positive charge is mainly located at the 1-position.

EXPERIMENTAL

The e.s.r. spectroscopic techniques, the pulse conductometric measurements, sample preparation, wet analysis, and most of the materials have been described previously.[1]

2-Dichloromethyl-1,3-dioxolan, b.p. 56° at 0.5 mmHg, was obtained from 1,1-diethoxy-2,2-dichloroethane (Fluka) and ethane-1,2-diol in a process analogous to that described [1] for the other materials. The low-boiling products (Table 2) were analysed by g.l.c. using a precolumn technique in order to prevent the bulk of the water from entering the main column:[14] precolumn, steel 1/8 in i.d., 3 m, 10% Marlophen 87 on Teflon; main column, steel, 1/8 in i.d., 3 m, 15% P 4000 on Celite; both columns at 100 °C. The higher boiling products (Table 8) were analysed on glass capillary columns, 26 m Carbowax 20 M, detector (f.i.d.) and injection block at 250 °C, column 50—250 °C, 5° min^{-1}, 0.8 atm. argon, sample 1.2 µl. Characteristic masses from mass spectra: peak no. 2 (Table 8), m/e 165, 105, and 75 ($C_3H_8O_5$); peak no. 3, *m/e* 181, 163, 149, 119, 103, 93, 75, 71, and 58; peak no. 4, *m/e* 123, 105, 93, 61, 45, and 43; peak no. 5, *m/e* 165, 147, 103, 93, 87, 59, and 43; peak no. 6, *m/e* 197, 183, 137, 107, 105, 93, and 75; peak no. 7, *m/e* 197, 183, 153, 137, 93, 73, 59, 58, and 43.

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