

## Formation and Structure of 1,1-Dialkoxyalkene Radical Cations in Aqueous Solution. An *in situ* Electron Spin Resonance and Pulse Conductivity Study

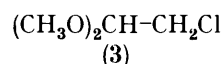
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The radical cations (1), (10), (11a and b), and (12)–(15) have been produced in aqueous solution and have been identified by e.s.r. spectroscopy and conductivity investigation. The open chain radical cations exist in *Z,E*-configurations. They exhibit two sets of  $a_{\beta}^H$  couplings. The larger couplings were assigned to the protons in groups with the *Z*-configuration. In all cases the radical spin is located mainly at the carbon atoms. Under our conditions radical (13) disappeared pseudo-monomolecularly upon reaction with water ( $k = 7 \times 10^3 \text{ s}^{-1}$ ) whereas the other radical cations are longer lived and decayed bimolecularly with diffusion controlled rates. The radical cations were generated from open chain or cyclic acetals bearing Br, Cl, or  $\text{CH}_3\text{CO}_2$  groups  $\beta$  to the acetal CH group, e.g.  $(\text{CH}_3\text{O})_2\text{CH}-\text{CH}_2\text{Cl}$  or  $(\text{CH}_2\text{O})_2\text{CH}-\text{CH}_2\text{Cl}$ . These substrates were subjected to hydrogen abstraction by  $\text{OH}^\cdot$  or  $\text{SO}_4^{\cdot-}$  radicals or triplet acetone in aqueous solution. Hydrogen abstraction from the acetal CH group led to radicals which undergo fast heterolytic dissociation into radical cations and leaving group anions, e.g.  $(\text{CH}_3\text{O})_2\dot{\text{C}}-\text{CH}_2\text{Cl} \longrightarrow (\text{CH}_3\text{O})_2\dot{\text{C}}-\dot{\text{C}}\text{H}_2 + \text{Cl}^-$ .

WURSTER'S Blue, now known for 100 years,<sup>1</sup> and identified first by Weitz<sup>2</sup> as a salt of the *NNN'*-tetramethyl-*p*-phenylenediamine radical cation is among the first examples of aromatic radical cations.<sup>3</sup> This species does not react with water because amino groups are present thus reducing the redox potential and decreasing the electrophilicity of the radical cation. Recently it was established that methoxy groups on the benzene ring stabilize radical cations to an extent which allows e.s.r. observation in aqueous solution and pulse radiolytic detection by u.v. and conductivity changes.<sup>4</sup> These radical cations do not react with water. In contrast to Wurster's Blue they disappear bimolecularly by reaction with each other. Also methyl groups are able to stabilize benzene radical cations to a degree.<sup>5</sup> With an increasing number of methyl groups a graduated and decreasing reactivity towards  $\text{H}_2\text{O}$  addition (yielding  $\text{H}^\cdot$  and hydroxycyclohexadienyl radicals) and deprotonation (yielding  $\text{H}^\cdot$  and benzyl radicals) was found.

As in the aromatic series ethylene-derived radical cations are rather stable if highly substituted by amino, alkylthio, or aromatic groups.<sup>3</sup> A systematic study of their reactivity towards water is lacking since their olefinic precursors are often moisture sensitive. E.s.r.

In the present paper it is shown that certain alkene radical cations which carry two geminal alkoxy-groups are sufficiently stable towards water to allow e.s.r. spectroscopic and pulse conductometric observations in aqueous solution. In a preliminary communication<sup>8</sup> we briefly reported evidence in aqueous solution on the existence of the 1,1-dimethoxyethylene radical cation (1) which was generated from radical (2) according to reaction (I). Radical (2) was obtained by hydrogen abstraction from 2-chloro-1,1-dimethoxyethane (3), by  $\text{OH}^\cdot$  or  $\text{SO}_4^{\cdot-}$  at position 1.



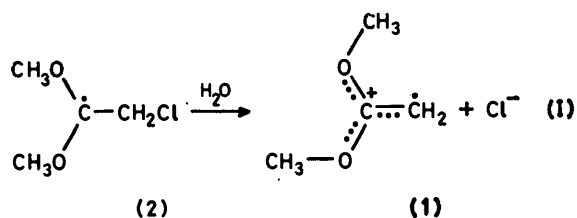
### RESULTS

Extending the above method for generating radical cation (1) to other  $\beta$ -substituted acetals we obtained a series of 1,1-dialkoxyalkene radical cations in aqueous solution. They show differences in structure and conformation which are discussed below.

*E.s.r. Spectroscopic Studies.*—*Radical cations.* For hydrogen abstraction from substrates, triplet acetone,  $\text{OH}^\cdot$ , or  $\text{SO}_4^{\cdot-}$  radicals from u.v. irradiation of acetone,  $\text{H}_2\text{O}_2$ , or  $\text{S}_2\text{O}_8^{2-}$  were employed. In this work most spectra were obtained by using aqueous solutions of 0.3M-acetone,  $10^{-2}\text{M}$ - $\text{K}_2\text{S}_2\text{O}_8$ , and ca.  $5 \times 10^{-2}\text{M}$ -substrate. Acetone enhanced the spectral intensity presumably by sensitizing the decomposition of  $\text{S}_2\text{O}_8^{2-}$  to  $\text{SO}_4^{\cdot-}$ .

From the substrates (4)–(9) the radical cations (10)–(15) were obtained (see Scheme).

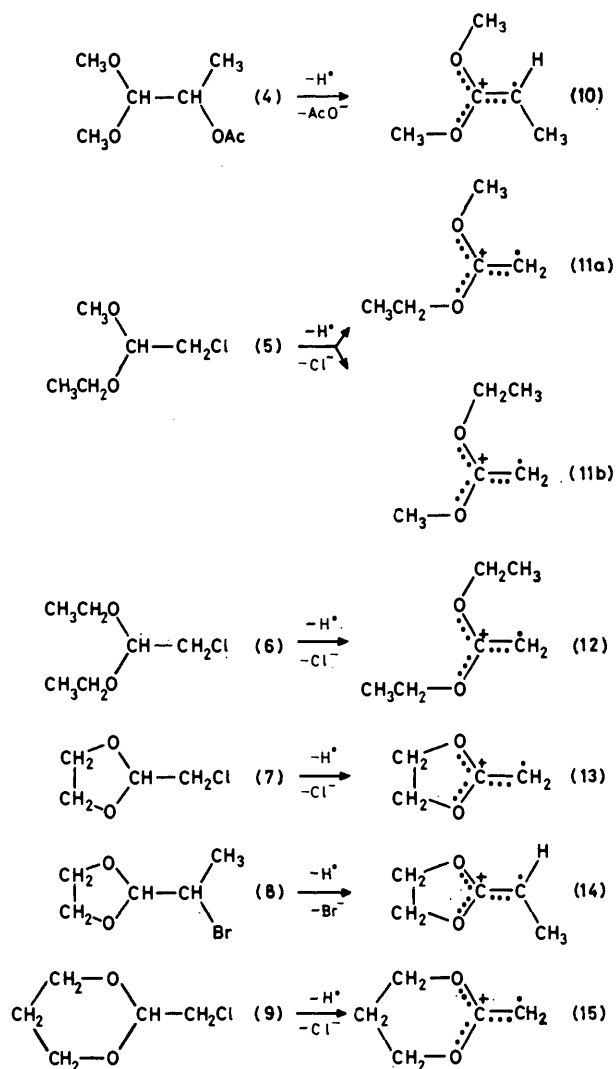
They are best observed in acidic solutions at  $\text{pH} < 5$ . The e.s.r. parameters of the radical cations are given in Table 1. Notably, the open chain radical cations exhibit two rather different couplings arising from the protons of two different alkoxy groups. Therefore, these species are assumed to be asymmetric. Two isomeric 1-ethoxy-1-methoxyethylene radical cations (11a and b), were observed, but only one isomer, (10), of the 1,1-dimethoxyprop-1-ene radical cation was detected. The 2-methylene-1,3-dioxolan radical cation (13), and the 2-methylene-1,3-dioxan radical



spectra of such radical cations have been recorded<sup>3,6</sup> mainly in  $\text{CH}_3\text{CN}$  or other solvents of low nucleophilicity. Substitution by alkyl substituents is also effective in stabilizing ethylene radical cations; however, only a few examples (in  $\text{CF}_3\text{CO}_2\text{H}$  as solvent) are known.<sup>7</sup>

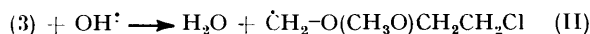
cation, (15), are symmetrical species. As to the assignment of couplings to specific protons see the Discussion section. The e.s.r. spectra of (10), (11a and b), (14), and (15) are given as examples in Figures 1—3.

*Other radicals.* Hydrogen abstraction from substrates (3)—(9) does not only occur at the acetal C-4 bond but also



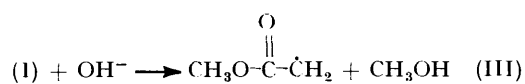
SCHEME

at the alkoxy groups. Four ether radicals resulting from such hydrogen abstraction, *e.g.* reaction (11), have been



identified e.s.r. spectroscopically (see Table 2). These radicals do not give rise to radical cations.

All radical cations, (1) and (10)—(15), react with  $\text{OH}^-$  to yield ester radicals, *e.g.* reaction (III), the e.s.r. spectra of which are well observed at pH values above the range given in Table 1.



*Attempts to observe the precursor radicals of the radical cations.* Similar to the radical (2) the related radicals

$\text{CH}_3\text{O}-\dot{\text{C}}\text{H}-\text{CH}_2\text{Cl}^9$  and  $\text{CH}_3\text{O}-\dot{\text{C}}\text{H}-\text{CH}_2-\text{PO}_4(\text{CH}_2\text{CH}_2-\text{OCH}_3)_2^{10}$  were not observable by e.s.r. spectroscopy in aqueous solution because they undergo fast hydrolysis. They have half-lives in water at  $0^\circ$  of  $\leq 20$  ns<sup>10</sup> compared with  $\geq 100$   $\mu\text{s}$  in acetone in which solvent they were well observable e.s.r. spectroscopically.<sup>10,11</sup> These radicals dissociate in aqueous solution into an anion and a radical cation (which is very short lived<sup>12</sup>) in close analogy to reaction (I). It was therefore attempted to observe by e.s.r. spectroscopy in acetone the precursor radicals of the radical cations of Table 1. However, they could not be

TABLE 1

E.s.r. parameters of dialkoxyalkene radical cations in aqueous solutions at  $3^\circ\text{C}$

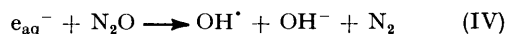
	Hyperfine splittings* (mT)	<i>g</i> factor	pH range †
(1)	0.066 0.310 2.055	2.003 05	1—8.6
(10)	0.073 0.284 2.452	2.003 11	2—9.6
(11a)	0.065 0.345 2.06	2.003 05	2—7
(11b)	0.067 0.316 2.06	2.003 05	2—7
(12)	0.061 0.336 2.063	2.003 05	1.4—6.3
(13)	0.245 2.057	2.003 08	1—7.3
(14)	0.245 0.258 1.870 2.511	2.003 19	2—9
(15)	0.337* 0.0083 2.076 0.337*	2.003 18	2—9

\* The number of protons is shown in the formulae. † Range of actual observations; the upper value is a limit. ‡ Mean value of non-equivalent hydrogens.

detected and it is assumed that they are still shorter lived with respect to heterolytic dissociation than, *e.g.*, the radical  $\text{CH}_3\text{O}-\dot{\text{C}}\text{H}-\text{CH}_2\text{Cl}$ .

*Conductivity Studies.—Introductory remarks.* For the conductivity studies 2.8 MeV electron pulses of 1 ns duration were applied. The electron pulses produce the following species in aqueous solution:  $\text{H}_2\text{O} \longrightarrow \text{OH}^\cdot, \text{H}^\cdot,$

$e_{aq}^-$ ,  $H_2O_2$ ,  $H^+$ , and  $OH^-$ . In the presence of  $N_2O$  the solvated electrons,  $e_{aq}^-$ , are converted into  $OH^\bullet$  radicals according to equation (IV). Using  $N_2O$ -saturated aqueous



solutions  $OH^\bullet$  radicals and hydrogen atoms are formed in the ratio of 9 : 1 and with a total yield of 6.6 radicals per 100 eV of energy absorbed<sup>13</sup> (100 eV yield =  $G$  value). The above radicals abstract hydrogen atoms from added substrates. Since hydrogen abstraction by  $OH^\bullet$  is very fast with ether-like substrates ( $k \geq 10^9$  l mol<sup>-1</sup> s<sup>-1</sup>), at concentrations of

of substrate-derived species in the  $\mu s$  range the transient conductivity changes produced in water alone have to be taken into consideration. This is done by subtracting the signals obtained in the absence of substrate from those obtained in the presence of substrate under otherwise identical experimental conditions. Conductivity curves corrected in this sense are presented below.

*Results of conductivity studies.* Using slightly acidic  $N_2O$ -saturated  $10^{-2}M$  aqueous solutions of substrates (3)–(9) there was (after application of the above corrections) a conductivity change immediately after the pulse (see Figure

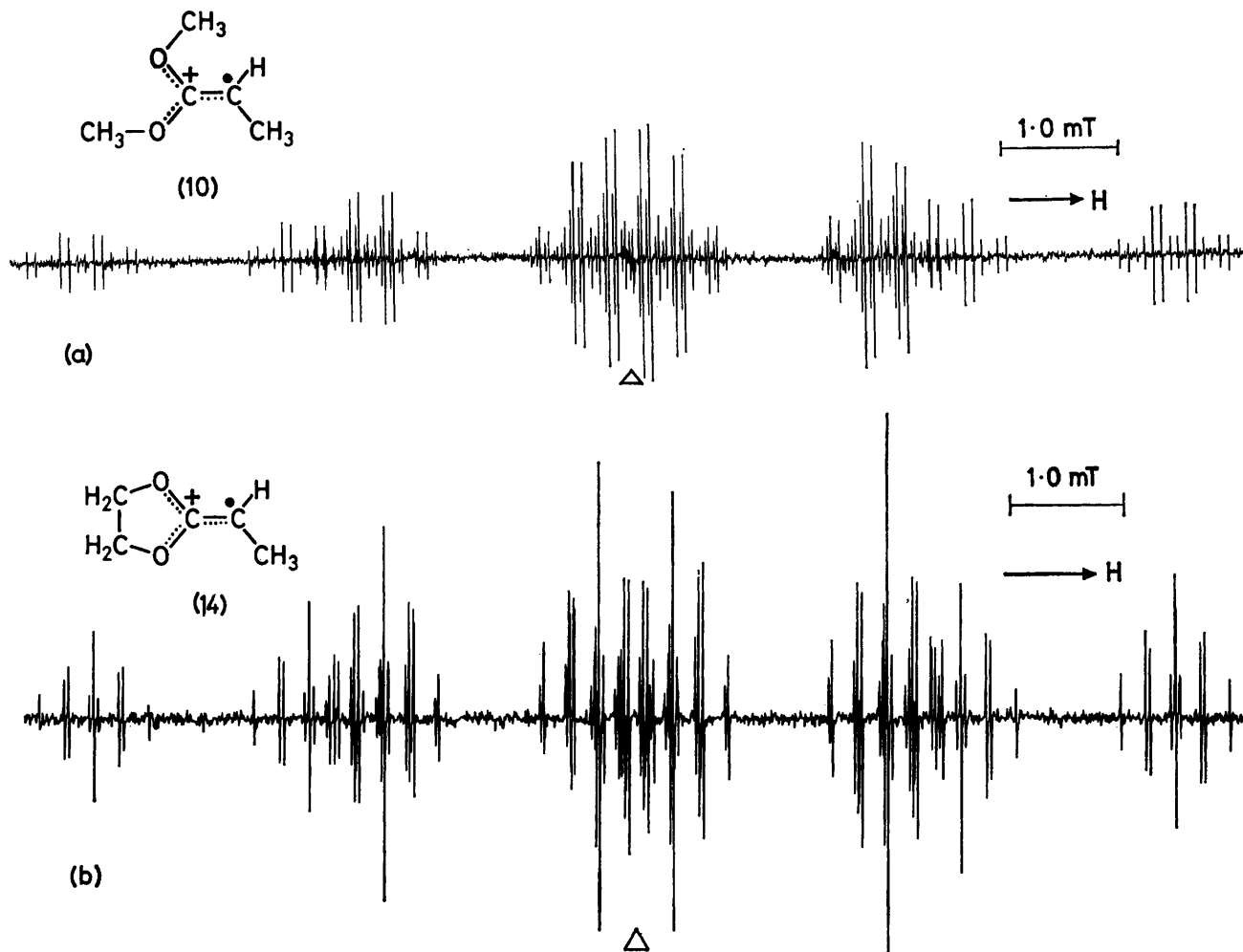


FIGURE 1 E.s.r. spectra of (a) the  $(Z,E)$ -1,1-dimethoxy- $(Z)$ -prop-1-ene radical cation (10) and (b) the 2-ethylidene-1,3-dioxolan radical cation (14); centres indicated by triangles. Both radical cations exhibit large  $CH_3$  splittings; note, *e.g.*, the well resolved second-order components. The size of the  $CH_3$  couplings, 2.452 for (10) and 2.511 for (14), indicates that the unpaired spin resides mainly at the carbon atom next to the  $CH_3$  group. Experimental conditions: photolytic flow system, aqueous solutions of pH 5 at 3 °C containing 0.3M-acetone, 0.02M- $K_2S_2O_8$ , and 0.03M-substrate: (a) 1,1-dimethoxy-2-acetoxypropane (4); (b) 2-(1-bromoethyl)-1,3-dioxolan (8)

$10^{-2}M$  of such substrates the organic radicals are produced practically within the duration of the microsecond pulse. The behaviour of the substrate radicals is then followed by measuring the time dependent conductivity changes. Since  $H^+$  and  $OH^-$  are also produced by the radiolysis of water there is always a transient conductivity right after the pulse which disappears on combination of  $H^+$  and  $OH^-$  within 100  $\mu s$  or shorter depending on pH and dose rate. In order to follow conductivity changes due to the chemical reactions

4a). There would have been no such conductivity change if only neutral radicals were formed. This conductivity is attributed to substrate ions produced during the 1  $\mu s$  pulse. The rate constant for the formation of the ions is therefore  $k \geq 10^6$  s<sup>-1</sup>. The formation of the immediate conductivity is followed by a second-order build up of a final and comparatively larger conductivity on the ms time scale using the substrates (3)–(6), (8), and (9) (*cf. e.g.* Figure 4b). A build-up similar in size but of first order with a half-life of *ca.* 80

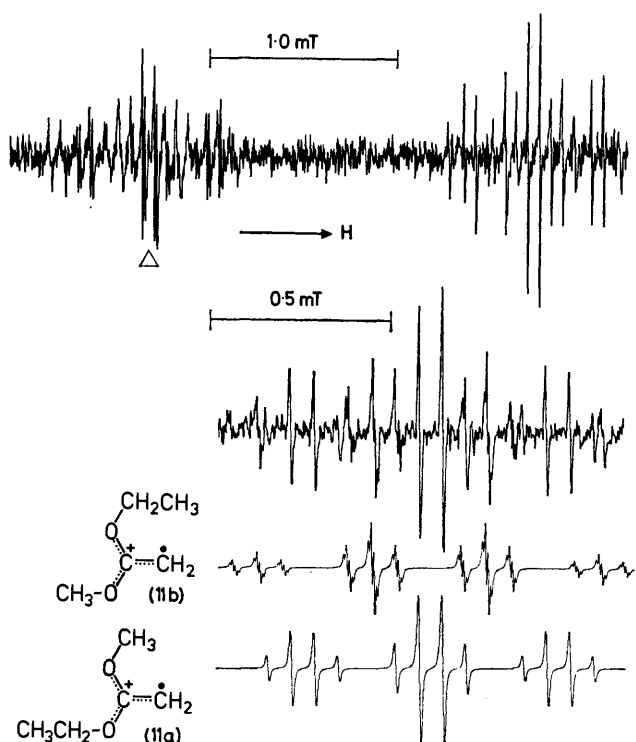


FIGURE 2 Upper figure: high field part of the e.s.r. spectrum of the (*Z*)-1-ethoxy-(*E*)-1-methoxyethylene radical cation (11a) and the (*E*)-1-ethoxy-(*Z*)-1-methoxyethylene radical cation (11b); centre indicated by a triangle. Second figure: expanded right hand section of the upper figure ( $m_1 = +1$  multiplet of the  $\dot{\text{C}}\text{H}_2$  group). Below are shown parts of the computer simulated spectra of (11b and a) using line widths of  $5 \mu\text{T}$ . From (11b) all splittings are resolved. In the spectrum of (11a) the non-resolved quartets of the  $\epsilon'$ -splittings appear as slightly broadened lines. The size of the  $\epsilon'$ -splittings (ca.  $0.003 \text{ mT}$ , Table 1) was derived by fitting the computed to the experimental line shapes. Experimental conditions: photolytic flow system, aqueous solution of  $0.04\text{M}$ - $\text{K}_2\text{S}_2\text{O}_8$  and  $0.03\text{M}$ -2-chloro-1-ethoxy-1-methoxyethane (5) at  $3^\circ\text{C}$  and pH 4. In this case the addition of acetone did not improve the signal to noise ratio

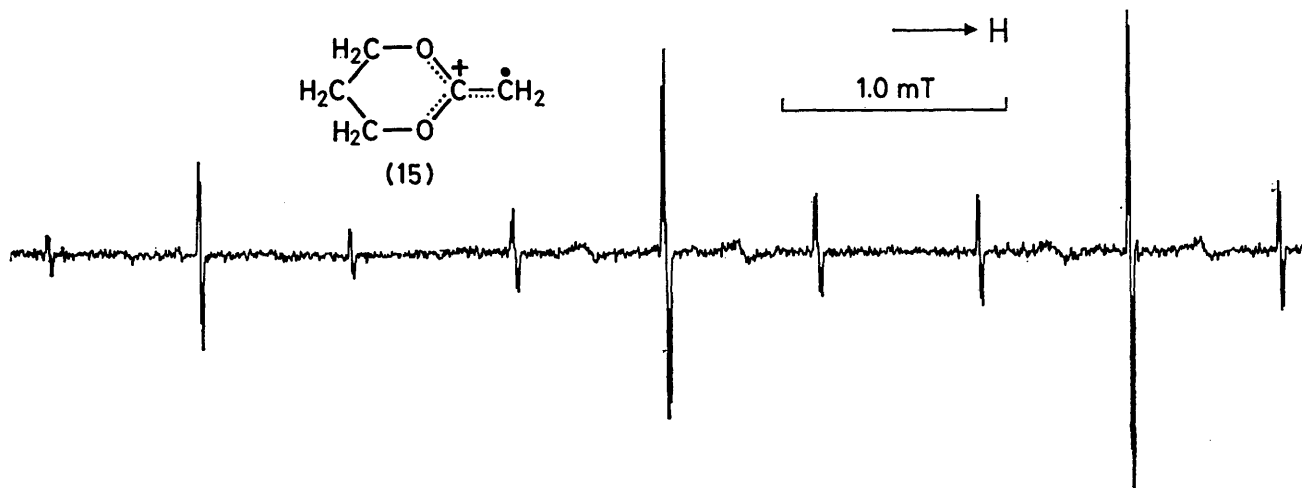
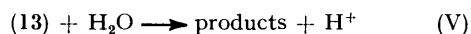


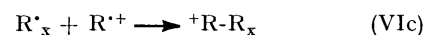
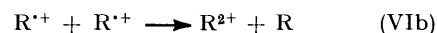
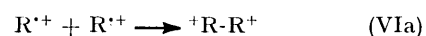
FIGURE 3 E.s.r. spectrum of the 2-methylene-1,3-dioxan radical cation (15). The distance between the central line and the outer lines of each of the three groups represents the sum of the splittings of the two pseudo-axial and the two pseudo-equatorial  $\delta'$  ring protons. Note the broadened lines from the conformational interconversions of the six-membered ring (see text). The non-broadened lines exhibit a small triplet from the two  $\epsilon'$  ring protons. Experimental conditions as in Figure 1, but with  $0.1\text{M}$ -2-chloromethyl-1,3-dioxan (9) as substrate

$\mu\text{s}$  at  $20^\circ\text{C}$  was observed using substrate (7) (see Figure 4c). These changes in conductivity are assigned to the replacement of moderately mobile radical cations by highly mobile protons. The equivalent conductances of the radical cations were determined to  $55 \pm 3 \text{ cm}^2 \Omega^{-1} \text{ M}^{-1}$  at  $20^\circ\text{C}$ ; they are ca. 6 times smaller than those of  $\text{H}^+$  at  $20^\circ\text{C}$ . The figures were derived by comparing the final conductivity changes with the immediate ones and using the known mobilities of  $\text{H}^+$  and the anions.

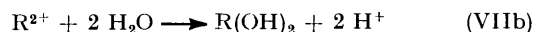
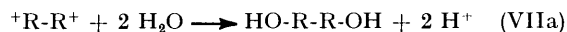
The first-order build up using substrate (7) is assigned to the reaction of the radical cation with water [reaction (V)]. The rate constant was determined to be  $k_V = 7 \times 10^9 \text{ s}^{-1}$  at  $20^\circ\text{C}$ .



The second-order build up of conductivity is assigned to the bimolecular termination of the radical cations,  $\text{R}^{\cdot+}$ . This may occur by dimerization or disproportionation of the radical cations with each other or with other radicals  $\text{R}'_x$  [see e.g. reactions (VI)]. In these reactions cations or



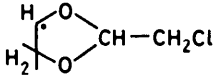
dications are formed which undergo fast reactions with water leading to the formation of protons [reactions (VII)]. The



first and second-order rate constants are listed in Table 3. Figure 4d shows the decay of radical cation (1) in alkaline solution due to the reaction of (1) with  $\text{OH}^-$  [ $k_{(\text{R}^{\cdot+} + \text{OH}^-)} = 4 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ , cf. reaction (III)].

*Effects in the presence of oxygen.* Using a mixture of  $\text{N}_2\text{O}$  and  $\text{O}_2$  in a molar ratio of 4 : 1 instead of  $\text{N}_2\text{O}$  alone for the saturation of the aqueous solutions containing one of the acetals (3)–(9), there was again conductivity present right

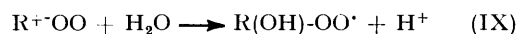
TABLE 2  
E.s.r. parameters of ether radicals obtained from selected acetals in aqueous solutions at 3 °C  
Hyperfine splittings (mT), number of protons in parentheses

Acetal	Radical	pH Range	$a_{\alpha}^H$	$a_{\beta}^H$	$a_{\gamma}^H$	Additional splittings	$g$ Factor
(3)	$\dot{\text{C}}\text{H}_2\text{O}-\text{CH}(\text{OCH}_3)\text{CH}_2\text{Cl}$	2-12	1.77 (2) *		0.072 (1)	$\delta(2)$ 0.018 $a_{\text{Cl}}$ 0.018	2.003 15
(4)	$\dot{\text{C}}\text{H}_2\text{O}-\text{CH}(\text{OCH}_3)\underset{\text{OC}(\text{O})\text{CH}_3}{\text{CH}}-\text{CH}_3$	2-11	1.78 (2) *		0.08 † (1)	$\delta(1)$ 0.02 ‡ OAc(3) 0.01 ‡	2.0031 ‡
(6)	$\text{CH}_3\dot{\text{C}}\text{HO}-\text{CH}(\text{OC}_2\text{H}_5)\text{CH}_2\text{Cl}$	1-10	1.45 (1)	2.28 (3)	†	†	2.0031 ‡
(7)		2-12	1.15 (1)	2.54 (1) 2.97 (1)	0.24 (1)	†	2.003 15

\* Mean value from non-equivalent hydrogens. † Not resolved. ‡ Low accuracy due to multiple line overlap.

after the pulse. Thereafter a first-order rise of conductivity occurred within a few  $\mu\text{s}$  which was followed by a second-order build up on the ms time scale (see Figure 4e). The initial dissociation of the precursor radicals according to or by analogy with reaction (I) is not inhibited by  $\text{O}_2$ , thus the dissociation is significantly faster than the addition of  $\text{O}_2$  to

the radical cations. The first-order rise of conductivity is assigned to the pseudo-first-order addition of  $\text{O}_2$  to the radical cations,  $k_{(\text{O}_2 + \text{R}^{\cdot+})} > 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ , by which reactions peroxy radical cations are formed which subsequently react with water with liberation of protons [see reactions (VIII) and (IX)]. The second-order rise of con-



ductivity is assigned to the formation of organic acids in analogy to related processes which were observed with dimethoxymethane as substrate.<sup>14</sup> The observed reactivity of the radical cations towards  $\text{O}_2$  is remarkable in view of the

TABLE 3

Kinetic data for the decay reactions of 1,1-dialkoxyalkene radical cations in aqueous solution. Data from pulse conductometric measurements at  $20 \pm 2$  °C, accuracy  $\pm 20\%$

Radical cation	$2k_{\text{term}}/\text{l mol}^{-1} \text{ s}^{-1}$	$k_{\text{obs.}}/\text{s}^{-1}$ ( $\text{R}^{\cdot+} + \text{H}_2\text{O}$ )
(1)	$1.8 \times 10^9$	
(10)	$7 \times 10^8$	
(11)	$1.8 \times 10^9$	
(12)	$2.0 \times 10^9$	
(13)		$7 \times 10^3$
(14)	$1.1 \times 10^9$	
(15)	$2.5 \times 10^9$	

non-reactivity of the anisole radical cation and related species<sup>15</sup> towards  $\text{O}_2$  during radical life under pulse radiolytic conditions. The reactions are under further study.

**Product studies.**  $^{60}\text{Co}$ - $\gamma$ -irradiation of  $\text{N}_2\text{O}$  saturated aqueous solutions of the acetals used in this work were performed in order to determine by argentometric titration the halides liberated according to reaction (I) and by potentiometry the proton to be expected according to reaction (IX). The  $G$  values of acid formation thus obtained are compiled in Table 4 together with the  $G$  values of proton formation derived from the pulse conductivity studies. There is good agreement between the three sets of data. The  $G(\text{H}^+)$  values divided by the  $G$  value of the initiator radicals [ $G(\text{OH}) + G(\text{H}) = 6.6$ ] gives the fraction of hydrogen abstraction that occurs at the acetal C-H position (*cf.* Table 4).

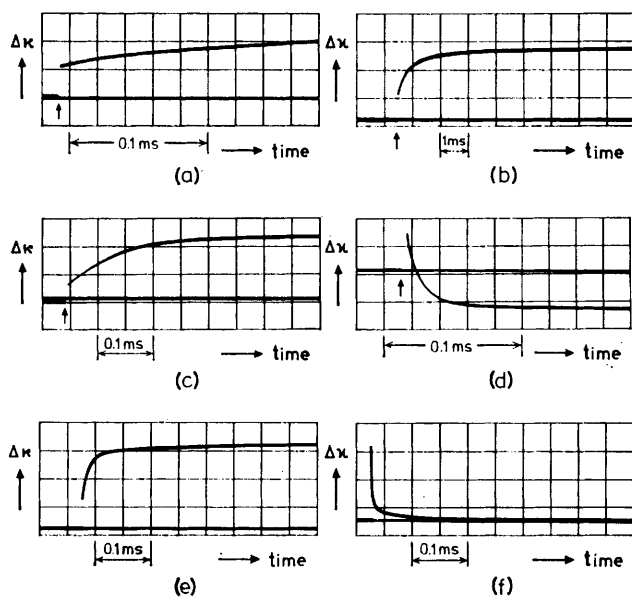


FIGURE 4 Conductivity changes observed after application of a  $1 \mu\text{s}$  electron pulse (2.8 MeV) to aqueous solutions, at  $20 \pm 2$  °C, of  $2 \times 10^{-3} \text{ M}$ -2-chloro-1,1-dimethoxyethane (3) or 2-chloromethyl-1,3-dioxolan (7); ordinates  $10 \text{ mV div}^{-1}$  in (b) and  $20 \text{ mV div}^{-1}$  in the other cases. (a)  $\text{N}_2\text{O}$ -Saturated solution of (3), pH 5, dose 6 Gy (0.6 krad); (b) second-order build up of conductivity,  $\text{N}_2\text{O}$ -saturated solution of (3), pH 5, dose 3 Gy (0.3 krad); (c) first-order build up of conductivity,  $\text{N}_2\text{O}$ -saturated solution of (7), pH 5, dose 3.1 Gy (0.31 krad); (d) decrease of conductivity,  $\text{N}_2\text{O}$ -saturated solution of (3), pH 9.3, dose 9.7 Gy (0.97 krad); (e) rise of conductivity, solution of (3), saturated with  $\text{N}_2\text{O}-\text{O}_2$  4 : 1, pH 5, dose 4.2 Gy (0.42 krad); (f)  $\text{N}_2\text{O}$ -saturated solution of 0.1M-propan-2-ol, pH 5, dose 5 Gy (0.5 krad). A transient signal is always observed even in the absence of acetal. It is due to the recombination of pulse produced  $\text{H}^+$  and  $\text{OH}^-$  plus some electrical disturbances, mainly during and up to  $20 \mu\text{s}$  after the pulse. Signals of that order of magnitude were subtracted from the original oscillograms (see text)

TABLE 4

$G$  values of  $H^+$  (column 2) and of halides, where applicable (column 3), as measured by potentiometric or argentometric titration, respectively, after  $^{60}\text{Co}$   $\gamma$ -irradiation of  $\text{N}_2\text{O}$ -saturated aqueous solutions, at  $0^\circ\text{C}$ , of *ca.*  $5 \times 10^{-3}\text{M}$  of the acetals used in this work and  $G(H^+)$  values (column 4) calculated from final conductivity changes after pulse radiolysis, at  $20 \pm 2^\circ\text{C}$  and  $\text{pH } 4.5\text{--}5$ . Dose rate of  $^{60}\text{Co}$   $\gamma$ -radiolysis  $1\,400\text{--}1\,600\text{ Gy h}^{-1}$  or  $140\text{--}160\text{ krad h}^{-1}$ , dose applied causing  $1\text{--}3\%$  conversion of acetals. Accuracy: column 2 and 3,  $\pm 5\%$ ; column 4,  $\pm 20\%$ . The fraction of hydrogen abstraction at the acetal C-H bond, is given in column 5 (*cf.* text)

Acetal	$G(H^+)$ After $^{60}\text{Co}$ $\gamma$ - radiolysis	$G(\text{halide})$	$G(H^+)$ From pulse conductivity	$f$
(3)	2.5	2.5	2.5	0.38
(4)	2.0		1.7	0.30
(5)	1.8	1.8	1.4	0.27
(6)	1.5	1.4	1.0	0.23
(7)	5.5*	5.5*	4.3	0.65*
(8)	3.9	3.9	4.1	0.59
(9)	2.9	3.1	2.8	0.44

\*  $G$  4.3, after correction for a chain contribution which was derived from dose rate effects.

## DISCUSSION

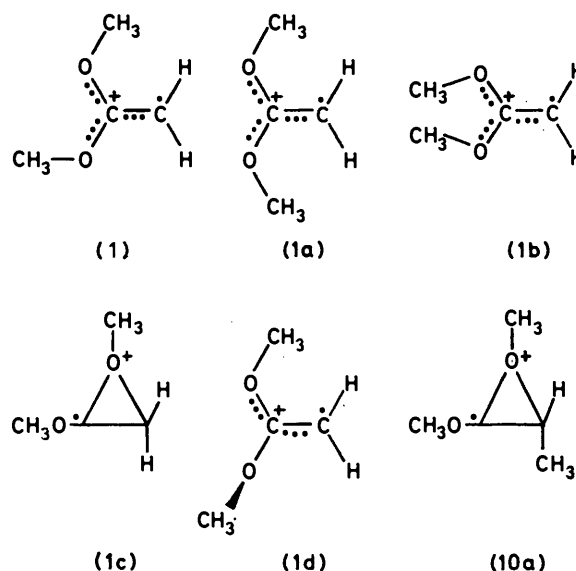
*The Existence of 1,1-Dialkoxyalkene Radical Cations in Aqueous Solutions.*—From the results presented above there is no doubt as to the existence of certain 1,1-dialkoxyalkene radical cations in aqueous solution. The completely resolved e.s.r. spectra give proof of halogen-free species containing an even number of hydrogen atoms, and the pulse conductivity measurements demonstrate the presence of charged species right after the pulse and the disappearance of these charged species producing a higher conducting species which is concluded to be a proton.

*Conformation of the Radical Cations.*—As to the conformation of the radical cation (1) the alternatives (1) and (1a–d) were considered. With the exception of (1d) all the conformations are planar. Conformation (1a and b) are excluded because they require equal  $\delta'$ -couplings which are not found. Structure (1c) is excluded by analogy with the radical cation (10) (*cf.* Scheme and Table 1). Structure (10a) is expected to have an  $a^{\text{CH}_3}$  coupling of *ca.* 0.07 mT and cannot have an  $a^{\text{CH}_3}$  coupling as large as observed. The size of this coupling and that of the  $\alpha$  splitting not only excludes structure (10a) but also indicates that in structure (10) around 80% of the spin density resides at the 2-position. Conformation (1d) is energetically disfavoured with respect to (1) by 8 kcal mol $^{-1}$  according to an INDO calculation performed by Noack and Olbrich.<sup>16</sup> For energetic reasons structures (1a and b) are also excluded by this calculation [structure (1c) was not considered therein]. The 1,1-dimethoxyethylene radical cation is then present in the  $Z,E$ -conformation (1). The strong  $a^{\text{CH}_3}$  coupling indicates that in (1) *ca.* 80% of the spin density is present at the 2-position, leading to a separation of charge and free spin. The charge is mainly con-

centrated at the  $(\text{CH}_3\text{O})_2\text{C}$  group. An analogous structure was assigned to the radical cation  $[(\text{CH}_3)_2\text{N}]_2\dot{\text{C}}\text{--}\dot{\text{C}}\text{H}_2$ .<sup>17</sup> The larger of the two  $\delta'$ -splittings of (1) is assigned to the alkoxy group in the  $Z$ -conformation which follows from the size of the  $\delta'$ -splittings of (13) and (14) (see Table 1). The INDO calculations lead to the same assignment and furthermore predict a small difference in the  $\text{CH}_2$  couplings of (1) which was actually observed as small selective line broadening.<sup>8</sup>

The other open chain radical cations are apparently also present in the  $Z,E$ -conformation. The identification of the two isomeric 1-ethoxy-1-methoxyethylene radical cations (11a and b), clearly indicates that there is no fast interconversion of the two species and that rotational barriers exist around the O-C-O bonds. With (1) the couplings did not change at  $50^\circ\text{C}$  and thus no equilibration was experimentally recognizable. From substrate (4) only one of two radical cations with a  $Z,E$ -conformation of the  $\text{OCH}_3$  groups, *viz.* the ( $Z,E$ )-1,1-dimethoxy-( $Z$ )-prop-1-ene radical cation (10) was obtained. The isomer with the ( $E$ )-prop-1-ene partial conformation is probably energetically disfavoured because of steric hindrance.

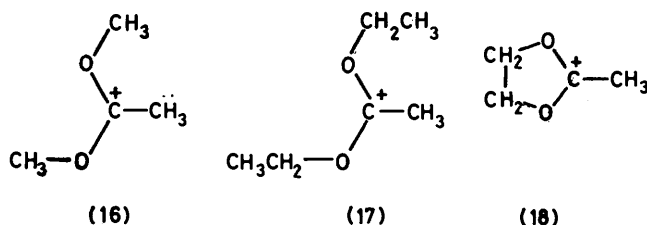
The structure of the 2-methylene-1,3-dioxolan radical cation (13) is highly symmetrical. There is a plane and



an axis of symmetry. From the e.s.r. spectrum of (13) (Table 1) it is concluded that the ring is either rigid or a fast conformational exchange occurs. The 2-methylene-1,3-dioxan radical cation (15) has an axis of symmetry. The e.s.r. spectrum (Figure 3) shows strong line width alternation from two sets of two equivalent protons. These are assigned to the pseudo-axial and pseudo-equatorial pairs of protons in the 4- and 6-positions. Due to this alternation only the sum of their individual splittings was observable. Therefore the mean value of the splittings is indicated in Table 1. The situation is considered typical of 'intermediate' interconversion rates of six-membered ring radicals.<sup>18</sup> On increasing the

temperature to 50 °C the broad lines sharpened and the pattern became nearly a quintet with a 1:4:6:4:1 intensity ratio, indicating increased exchange rates. The 2-ethylidene-1,3-dioxolan radical cation (14) is asymmetric as shown by its e.s.r. spectrum (Figure 1b). The assignment of couplings to specific ring protons (Table 1), is preliminary; the structure needs further investigation. The large CH<sub>3</sub> coupling is indicative of the spin being localized mainly at position β to the CH<sub>3</sub> group.

*Comparison with the Conformation of Related Cations.*— There are analogies between the conformation of the radical cations (1), (12), and (13) and the corresponding cations (16)—(18). The cations (16)<sup>19,20</sup> and (17),<sup>21</sup> like



the radical cations (1) and (12), are asymmetrical as judged from n.m.r. data, and analogous *Z,E*-conformations were assigned to them. The cation (18) is assumed from n.m.r.<sup>22</sup> and other data<sup>23</sup> to be rigid and planar;<sup>23</sup> planarity is also in accord with the spectroscopic data of the radical cation (13). It seems, therefore, that the driving force for the attainment of the conformations is the same in both series.

#### EXPERIMENTAL

2-Chloro-1,1-dimethoxyethane (3) and 2-chloro-1,1-diethoxyethane (6) were commercially available and were purified by fractionation *in vacuo*. 2-Chloromethyl-1,3-dioxolan (7) and 2-chloromethyl-1,3-dioxan (9) were obtained by known procedures<sup>24</sup> from (3) by treatment with ethane-1,2-diol or propane-1,3-diol, respectively, and concentrated H<sub>2</sub>SO<sub>4</sub> as catalyst, separation of methanol by distillation, neutralization of the catalyst by Na<sub>2</sub>CO<sub>3</sub>, and subsequent fractionation. 2-Chloro-1-methoxy-1-ethoxyethane (5) was obtained analogously, using ethanol instead of the diols, b.p. 31 °C at 4 mmHg. 2-(1-Bromoethyl)-1,3-dioxolan (8) was prepared from 2-bromo-1,1-diethoxypropane (ICN) and ethane-1,2-diol, b.p. 56 °C at 5 mmHg. 2-Acetoxy-1,1-dimethoxypropane (4) was prepared by reaction of acetyl chloride with 1,1-dimethoxypropan-2-ol in ether in the presence of pyridine, separation of py·HCl, and work-up by distillation, b.p. 72 °C at 15 mmHg. 1,1-dimethoxypropan-2-ol was prepared from 1,1-dimethoxypropan-2-one (Merck) by reduction with NaBH<sub>4</sub> in water at room temperature, b.p. 82 °C at 50 mmHg.

All the acetals were ≥99.7% pure according to g.l.c. analysis. Their structure was confirmed by elemental analysis and n.m.r. spectroscopy.

Water was triply distilled. N<sub>2</sub>O was freed from O<sub>2</sub> by passing it over a Chromosorb column (Messer-Griesheim, Duisburg). Other chemicals were of analytical grade.

E.s.r. spectra were measured under *in situ* photolysis conditions at the X-band with 100 kHz modulation using a flow technique at variable temperatures.<sup>25</sup> The standard flow rate of the aqueous solutions was 0.1 cm<sup>3</sup> s<sup>-1</sup> for an 0.3 × 8 mm<sup>2</sup> cross section of the cell. Considerably higher flow rates were occasionally used to eliminate problems arising from pH drift.

The absolute errors of the *g* factors and of the coupling constants are ±2 × 10<sup>-5</sup> and ±5 μT respectively. The measurements were performed with a n.m.r. sideband technique<sup>25</sup> taking into account the field offset of the n.m.r. probe, that was attached to the side wall of the cavity, and the second-order corrections.<sup>26</sup>

The conductivity measurements in combination with pulse radiolysis,<sup>27</sup> the sample preparation for <sup>60</sup>Co γ-radiolysis,<sup>27</sup> and the analytical procedures<sup>28</sup> have been described.

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