

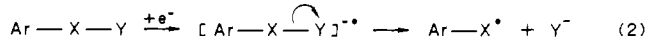
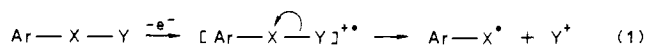
# Lifetimes of $\alpha$ -Dialkoxy Carbocations Produced via Radical Cations Generated by Electron Transfer and Photoionization in Aqueous Solution

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**Abstract:** One-electron oxidation of acetals  $\text{PhCH}_2\text{CR}(\text{OR}')_2$  by reaction with photolytically produced  $\text{SO}_4^{\bullet-}$  or by biphotonic photoionization ( $\lambda = 248 \text{ nm}$ ) in aqueous solution leads to the benzyl radical  $\text{PhCH}_2^\bullet$  and to  $\alpha$ -dialkoxyethyl carbocations  $\text{RC}^+(\text{OR}')_2$ . The reaction proceeds via a radical cation intermediate which undergoes rapid ( $k \geq 7 \times 10^7 \text{ s}^{-1}$ ) heterolytic C-C fragmentation. The cations thus formed react with water with rate constants  $k(\text{H}_2\text{O})$  which have been measured by time-resolved conductance ( $\text{R} = \text{H, alkyl, Ph}$ ) and optical ( $\text{R} = \text{Ph}$ ) methods. A total of 24 acyclic and cyclic cations have been kinetically characterized, with values of  $k(\text{H}_2\text{O})$  ranging from  $4.6 \times 10^7 \text{ s}^{-1}$  (4,4,5,5-tetramethyl-1,3-dioxolan-2-ylum) to  $8.6 \times 10^2 \text{ s}^{-1}$  (2-phenyl derivative of the above cation). Replacement of  $\text{R} = \text{H}$  by methyl leads to an increase in the lifetime by a factor of about 1000. However, the substitution of  $\text{R} = \text{Me}$  by bulkier alkyl groups (e.g. tBu) does not further kinetically stabilize (in the case of the cyclic cations) or it even destabilizes the cations (with the acyclic systems). The effect of  $\text{R} = \text{Ph}$  depends on whether the cation is cyclic or acyclic: In the acyclic case steric interaction between the ortho hydrogens of the phenyl ring and the  $\text{OR}'$  substituents prevents complete coplanarity at  $\text{C}_\alpha$  as a result of which charge delocalization to the phenyl ring becomes less efficient, i.e. the kinetic stability of the cation is not increased relative to the cation with  $\text{R} = \text{Me}$ . In the case of the sterically uncongested cyclic systems, Ph leads to an increase of stability compared to Me. A heterolytic C-C fragmentation of an electronically excited neutral compound to a carbanion and a carbocation has also been characterized, with the acetals 2-phenyl-2-(*x*-nitrobenzyl)-1,3-dioxolane ( $x = \text{para or meta}$ ).

The one-electron oxidation of substituted aromatics often leads to oxidative transformation of the substituent, such as deprotonation or C-C fragmentation,<sup>3-12</sup> even though the primary oxidation step involves removal of an electron from the aromatic part of the molecule and not from the substituent. The (heterolytic) fragmentation results in separation of charge and spin (eq 1), a reaction type that is reciprocal to that observed<sup>13</sup> with



radical anions (eq 2). In order for reaction 2 to be rapid, Y has to be a good nucleofugal leaving group, which practically excludes

Y from being a carbon. This reaction is therefore not a general way to achieve fragmentation of a C-C bond. In contrast to this is reaction 1, where the electron pair<sup>14</sup> joining X and Y goes not to Y but to X. Here X can be a hetero atom or a carbon, and Y is typically hydrogen, but it can be carbon, so reaction 1 does represent a method to achieve C-C fragmentation.

It is the purpose of this paper to (a) provide further information on reaction 1 and (b) to utilize this reaction in order to study the reactivity of the so-formed cations  $\text{Y}^+$ . Simple dialkoxy- and trialkoxyalkyl cations have recently been produced and their reactions in aqueous solutions have been investigated<sup>15,16</sup> using a radiation-chemical "stepwise hydride removal" technique, which involves producing by H abstraction an  $\alpha$ -alkoxyalkyl radical followed by its one-electron oxidation to give the cation. However, the time resolution of this method is restricted by the fact that both formation and oxidation of the radical are via bimolecular reactions the maximum rates of which are dependent on the maximum achievable concentrations of the reactants. In practice, cations with lifetimes  $\leq 100 \text{ ns}$  are not easily accessible by this method. Another restriction is that phenyl-substituted carbocations cannot be generated, because the OH radical used to abstract H reacts with aromatic systems by addition and not by H abstraction from the substituent. Reactive cations have previously been produced by Dorfman and co-workers,<sup>17</sup> with a radiation-chemical approach involving the fragmentation of radical cations of organomercurials (analogous to eq 1 with  $\text{X} = \text{Hg}$ ).<sup>18</sup> However, with this method it is not possible to work in ionizing or nucleophilic solvents. Carbocation formation in such solvents has been achieved with a photoheterolytic approach involving ox-anions as nucleofugal groups.<sup>19</sup> The latter, however, is less

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practical for the study of dialkoxycarbocations since the necessary precursors  $\text{RC}(\text{OR}')_2\text{Y}$ ,  $\text{Y}^- = \text{oxyanion}$ , are unstable.

An attempt was therefore made to produce cations via a unimolecular reaction starting from stable and easily accessible precursors. A suitable path is indicated by eq 1, and in the following it will be shown that this method can be applied successfully to the production of aliphatic and aromatic dialkoxycarbocations, thus allowing the properties of these highly reactive intermediates to be studied under "solvolytic conditions". These intermediates are generally assumed to be formed in acid catalyzed solvolysis reactions of acetals and ortho esters,<sup>20</sup> and are models for the transient hydroxyalkyl carbocations produced in acid catalyzed ester solvolyses.

### Experimental Section

Acetals which were not commercially available were prepared following standard procedures. Dimethyl acetals, diethyl acetals, and phenylacetaldehyde diisopropyl acetal were prepared by mixing the aldehyde or ketone with an equivalent amount of the appropriate trialkyl orthoformate in the presence of a trace of *p*-toluenesulfonic acid.<sup>21</sup> After standing for 1 day, anhydrous potassium carbonate was added, and the mixture was fractionally distilled at reduced pressure. 1,3-Dioxolanes and 1,3-dioxanes were prepared by refluxing in benzene a mixture of the ketone, diol, and a trace of *p*-toluenesulfonic acid with removal of the water with a Dean-Stark trap.<sup>22</sup> After 1 day the cooled reaction mixture was extracted with aqueous sodium hydroxide, the benzene layer was dried with magnesium sulfate, and after removal of the benzene, the acetal was obtained by reduced-pressure distillation or recrystallization. 4,4,5,5-Tetramethyl-1,3-dioxolanes were prepared by stirring the aldehyde or ketone and pinacol in 85% phosphoric acid for 2 days.<sup>23</sup> Workup involved separation of the organic phase, followed by washing with aqueous sodium bicarbonate, drying with magnesium sulfate, and recrystallization or reduced-pressure distillation. The benzyl alkyl ketones which serve as precursors for the ketals were prepared by addition of the appropriate aldehyde to a commercial solution of benzylmagnesium chloride in ether. After standard workup the crude alcohol was oxidized to the ketone with chromiumtrioxide in acetone.<sup>24</sup> Trimethyl ortho-phenylacetate was prepared by using the anilide acetal procedure.<sup>25</sup> All compounds had the expected <sup>1</sup>H NMR spectra. The mass spectra are characterized by extensive fragmentation of the molecular ions with a strong preference for formation of the dialkoxycarbocations rather than the benzyl cation. New compounds gave satisfactory elemental analyses.

The solutions were prepared (using water purified with a Millipore Milli-Q system) by adding the substrates to deoxygenated water-acetonitrile solutions whose pH was preset at ~9 in order to prevent hydrolysis. The solutions (OD/cm  $\approx$  0.2–2) were then photolyzed with 20-ns pulses (5–100 mJ) of 248 nm (KrF\*) light from a Lambda Physik EMG103MSC excimer laser, with a flow system (flow rate  $\approx$  100 mL/h). The optical absorption or conductance signals were digitized with a Tektronix 7612 or 7912 transient recorder interfaced with a DEC LSI 11/73+ computer which was also used for process control of the apparatus and to on-line (pre)analyze the experimental data.<sup>26</sup> Final data analysis was performed with a Microvax II connected by Ethernet with the LSI. In a few cases experiments were performed in acid solution, with DC conductance detection. The basic solution of the acetal (pH  $\approx$  9 and containing  $\approx$  50 mM  $\text{CH}_2\text{Cl}_2$  to scavenge  $\text{e}^-_{\text{aq}}$ ) was acidified to pH  $\approx$  4 by mixing with an acidic solution immediately before reaching the site of photolysis, with a flow system. The transfer time from the mixing port to the electrodes was  $\leq$  1 s.

Pulse radiolysis and in situ photolysis ESR experiments were performed as previously described.<sup>27,28</sup>

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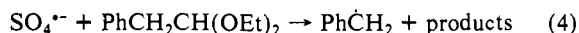
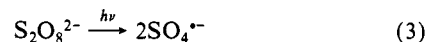
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### Results and Discussion

**1. Reactions with the One-Electron Oxidant<sup>29</sup>  $\text{SO}_4^{\cdot-}$ .** **a. In Situ Photolysis Electron Spin Resonance Experiments.** Aqueous solutions containing 20% (v/v) acetone,<sup>31</sup> 20 mM  $\text{K}_2\text{S}_2\text{O}_8$ , and 10 mM borate buffer (pH  $\approx$  9.2) were saturated with  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OEt})_2$  and photolyzed, while flowing through the flat quartz cell in the ESR cavity. Under these conditions  $\geq$ 99% of the light is absorbed by the acetone and the  $\text{S}_2\text{O}_8^{2-}$  ion undergoes homolysis to yield two  $\text{SO}_4^{\cdot-}$  ions, eq 3. The  $\text{SO}_4^{\cdot-}$  radical then



reacts with the organic substrate,<sup>32</sup> eq 4.<sup>33</sup> The high-field part of the spectrum obtained is shown in Figure 1. The spectrum is that of the benzyl radical, as can be shown by comparison of the coupling parameters with literature values<sup>34</sup> or by producing  $\text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2$  by alternative routes (e.g., photolysis of  $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{CH}_3$  or  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{CO}$  or reaction of  $\text{SO}_4^{\cdot-}$  with toluene<sup>11</sup> at pH = 1).

**b. Laser- and Pulse-Radiolysis Experiments with Optical and Conductance Detection.** Aqueous solutions containing 50% (v/v) acetonitrile (to solubilize the aromatic),<sup>35</sup> 100 mM  $\text{K}_2\text{S}_2\text{O}_8$ , and  $\approx$  1 mM  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OEt})_2$  and 10 mM borate buffer, pH  $\approx$  9.2, were photolyzed with 20-ns pulses of 248-nm light. Under these conditions  $>$ 90% of the light is absorbed by  $\text{S}_2\text{O}_8^{2-}$ , which homolyzes (eq 3). In agreement with this, the absorption spectrum recorded immediately after the pulse was found to be that of  $\text{SO}_4^{\cdot-}$  ( $\lambda_{\text{max}} = 450 \text{ nm}$ <sup>36</sup>). In the presence of  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OEt})_2$  this spectrum was replaced with first-order kinetics to give rise to a new spectrum with  $\lambda_{\text{max}}$  values at 260, 295, 305, and 315 nm. The rate of this reaction was found to depend upon the concentration of the aromatic and from this dependence the rate constant for its reaction with  $\text{SO}_4^{\cdot-}$  was determined to be  $1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . The rate constant increases with increasing water content to  $7.0 \times 10^8$  in water-acetonitrile (W-AN) 2:1 (v/v), to  $1.5 \times 10^9$  in W-AN 4:1, and to  $3.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in pure water, indicating a polar nature of the transition state of the  $\text{SO}_4^{\cdot-}$  reaction with the aromatic. The spectra recorded in pure water are shown in Figure 2: At 80 ns after the pulse, the spectrum shows a mixture of  $\text{SO}_4^{\cdot-}$  and benzyl radical. Reaction of  $\text{SO}_4^{\cdot-}$  leads to further production of  $\text{PhCH}_2^{\cdot}$  (see insets). The presence of the benzyl radical is particularly clearly documented by the fingerprint part in the region 290–320 nm ( $\lambda_{\text{max}} = 295, 305, \text{ and } 315 \text{ nm}$ ).  $\text{PhCH}_2^{\cdot}$  can also be produced by photolysis of  $\text{C}_6\text{H}_5\text{CH}_2\text{COCH}_3$ , or on reaction of  $\text{SO}_4^{\cdot-}$  with phenylacetic acid<sup>11</sup> (spectrum c, Figure

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(29) The  $\text{SO}_4^{\cdot-}$  radical may not react with benzene derivatives by outer sphere electron transfer, but by an inner-sphere path, i.e. addition/elimination (cf. Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer: Berlin, 1987; p 89 and Steenken, S. In *Free Radicals: Chemistry, Pathology and Medicine*; Rice-Evans, C., Dormandy, T., Eds.; Richelieu Press: London, 1988; p 51). All the presently available evidence, however, supports the assumption that reaction of  $\text{SO}_4^{\cdot-}$  with alkylated benzenes leads to their rapid one-electron oxidation (cf. ref 4–6, 11, and 30a).

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(31) The function of acetone is to increase the solubility of the acetal and to sensitize the photochemical decomposition of  $\text{S}_2\text{O}_8^{2-}$ .

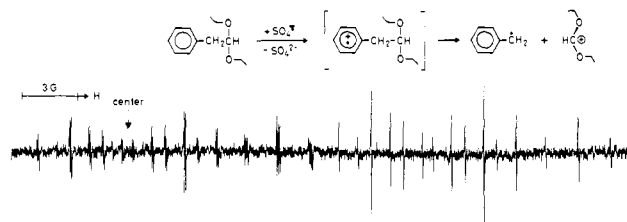
(32) For a collection of rate constants for  $\text{SO}_4^{\cdot-}$  reactions, see: Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027.

(33) A blank experiment was carried out by leaving out  $\text{K}_2\text{S}_2\text{O}_8$  from the solution under photolysis. Under these conditions the benzyl radical was absent. This proves that it is the  $\text{SO}_4^{\cdot-}$  radical which is involved in producing  $\text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2$ .

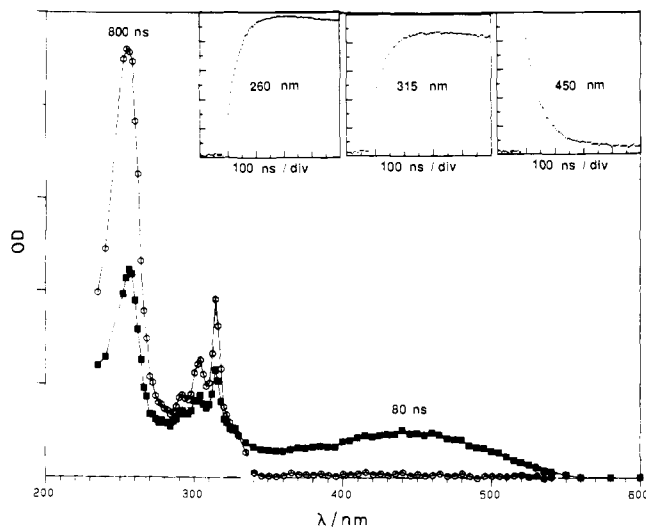
(34) Landolt-Börnstein, *Zahlenwerte und Funktionen aus Naturwissenschaften und Technik*, NS; Springer: Berlin, 1977; Vol. 9b, p 543.

(35) The lifetime of  $\text{SO}_4^{\cdot-}$  in acetonitrile-water mixtures is comparable to that in  $\text{H}_2\text{O}$ , showing the inertness of this electrophilic radical toward the electron-deficient acetonitrile.

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**Figure 1.** High-field part of the ESR spectrum of  $\text{Ph}\dot{\text{C}}\text{H}_2$  produced at  $\sim 4^\circ\text{C}$  on photolysis of 20 mM  $\text{K}_2\text{S}_2\text{O}_8$  in the presence of  $\text{PhCH}_2\text{CH}(\text{OEt})_2$  (saturated) in water-acetone 4:1 (v/v) at  $\text{pH} = 9.3$  (10 mM borate buffer).



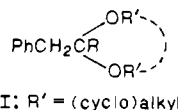
**Figure 2.** Absorption spectra recorded on 248-nm photolysis of 0.1 M  $\text{K}_2\text{S}_2\text{O}_8$  in  $\text{H}_2\text{O}$  in the presence of  $\text{PhCH}_2\text{CH}(\text{OEt})_2$  (saturated), 10 mM borate buffer  $\text{pH} = 9.2$ . The squares represent data recorded at 80 ns after the pulse. The circles represent data recorded 800 ns after the pulse. The insets show the decay of  $\text{SO}_4^{\bullet-}$  (at 450 nm) and the resulting formation of the benzyl radical as monitored at 260 and 315 nm.

3). These results thus confirm those obtained by ESR (eq 4).

If the spectrum from the reaction of  $\text{SO}_4^{\bullet-}$  with  $\text{PhCH}_2\text{CH}(\text{OEt})_2$  is compared with that from the interaction with  $\text{PhCH}_2\text{CO}_2\text{H}$  (Figure 3c), it is evident that with the former system the three benzyl bands at 295–315 nm sit on top of a broad band with  $\lambda_{\text{max}} = 290\text{--}320$  nm. This band is due to hydroxycyclohexadienyl type radicals derived by water addition to the radical cation (eq 5b) as concluded from a comparison with a spectrum obtained by reacting  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OEt})_2$  in aqueous solution at  $\text{pH} \approx 9$  with the  $\cdot\text{OH}$  radical, produced by 248-nm photolysis of 0.1 M  $\text{H}_2\text{O}_2$  or by pulse radiolysis.

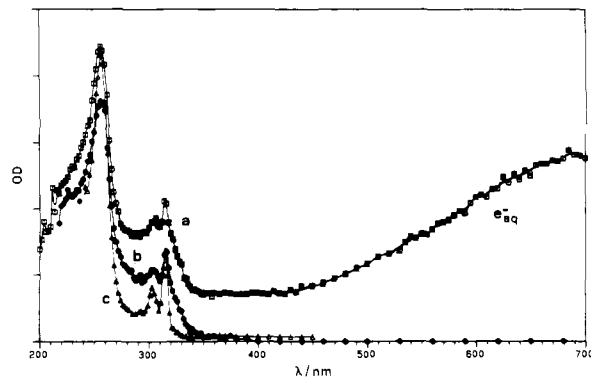
Further evidence that the bands in the 250–350-nm region are due to radicals is the quenching effect of oxygen: Addition of  $\text{O}_2$  to the solution leads to rapid decay of the benzyl bands at 260 and 295–315 nm and decay of the OH adduct bands at  $\approx 310$  nm, leaving a broad and relatively weak band at  $\sim 250$  nm which is presumably due to peroxy radicals.

Experiments analogous to those described for  $\text{PhCH}_2\text{CH}(\text{OEt})_2$  were performed with other benzyl-substituted acetals (structure I,  $\text{R} = \text{H}$  or alkyl; see Table I). In all cases, the benzyl radical

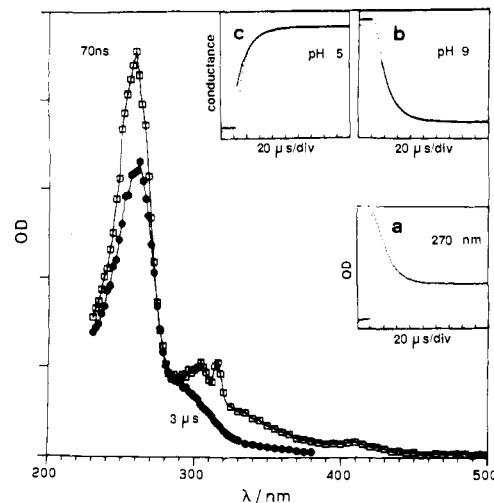


was a product of their reaction with  $\text{SO}_4^{\bullet-}$ . Hydroxycyclohexadienyl radicals ( $\lambda_{\text{max}} \approx 290\text{--}320$  nm) were also formed.

Experiments were also conducted with *phenyl*-substituted benzyl acetals (I,  $\text{R} = \text{Ph}$ ). In these cases it was found that although the absorption of the benzyl radical at 295–315 nm could be fully quenched by addition of  $\text{O}_2$ , that at 260 nm was reduced by only 30–50%, the remaining band decaying much slower and with a



**Figure 3.** Absorption spectra observed on 248-nm photolysis of a saturated solution of  $\text{PhCH}_2\text{CH}(\text{OEt})_2$  in water containing 10 mM borate at  $\text{pH} = 9.2$ : (a) recorded at 70 ns in the absence of an  $e_{\text{aq}}^-$  scavenger, (b) recorded at 70 ns in the presence of 0.1 M  $\text{CH}_2\text{Cl}_2$ , and (c) spectrum of  $\text{Ph}\dot{\text{C}}\text{H}_2$  obtained by reaction of  $\text{SO}_4^{\bullet-}$  with  $\text{PhCH}_2\text{CO}_2^-$  at  $\text{pH} \approx 6$ .



**Figure 4.** 248-nm photolysis of a saturated solution of  $\text{PhCH}_2\text{C}(\text{OCH}_2\text{CH}_2\text{O})\text{Ph}$  in water at  $\text{pH} = 9.2$  in the presence of  $\text{O}_2$  (1 mM). The spectrum recorded 70 ns after the pulse is due to  $\text{Ph}\dot{\text{C}}\text{H}_2$  and  $\text{PhC}^+(\text{OCH}_2\text{CH}_2\text{O})$ . That recorded 3  $\mu\text{s}$  after the pulse is due to  $\text{PhC}^+(\text{OCH}_2\text{CH}_2\text{O})$  (and, to a small degree, to  $\text{PhCH}_2\text{O}_2^{\bullet}$ ). The insets show the hydrolysis of the cation: the decrease of its concentration as monitored at 270 nm and the resulting production of  $\text{H}^+$  (at  $\text{pH} = 5$ ), which leads to a depletion of  $\text{OH}^-$  (at  $\text{pH} = 9$ ).

rate independent of  $[\text{O}_2]$ , which suggests that the species involved in not a radical. An example for this is shown in Figure 4, which relates to the cyclic acetal I ( $\text{R} = \text{Ph}$ ,  $\text{R}', \text{R}'' = -\text{CH}_2\text{CH}_2-$ ), oxidized by photoionization (see section 2). The spectrum recorded at 70 ns after the laser pulse in  $\text{O}_2$ -saturated aqueous solution is characterized by the typical benzyl peaks at 260, 305, and 315 nm. At 3  $\mu\text{s}$  the 305 and 315 bands have disappeared (due to reaction with  $\text{O}_2$ ), whereas that at 260 nm is still present. However, this band decays on a longer time scale by first-order kinetics (monitored at 270 nm; see inset a in Figure 4). Photolysis experiments with time resolved conductance detection showed that on the same time scale is occurring a decrease of conductance if the  $\text{pH}$  is  $> 7$  (as seen in inset b). The polarity of the conductance change is inverted (i.e. the decrease becomes an increase; see inset c) if the  $\text{pH}$  is  $< 7$ . This means that the product of the decay reaction of the species absorbing at 260 nm is a proton, which, in basic solution, removes 1 equiv of  $\text{OH}^-$ , thereby causing the conductance decrease. If the species produces a proton, it likely carries a positive charge. The species is identified as the 2-phenyl-1,3-dioxolan-2-ylum ion. This assignment is strongly supported by the fact that the absorption spectrum with  $\lambda_{\text{max}}$  at  $\sim 260$  nm is essentially the same as that<sup>37</sup> of a sample of the authentic cation isolated as a solid borofluorate salt.

As seen with the insets a–c, the rate constant for decay of the cation as measured optically is the same as that for production

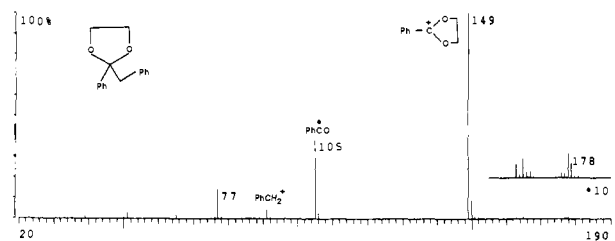
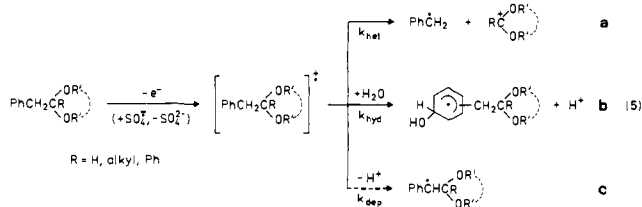


Figure 5. Mass spectrum of  $\text{PhCH}_2\text{C}(\text{OCH}_2\text{CH}_2\text{O})\text{Ph}$ . Ionization was by 70-eV electrons.

of  $\text{H}^+$  at  $\text{pH} = 5$  or that for removal of  $\text{OH}^-$  at  $\text{pH} = 9$ . These rates are independent of oxygen or the concentration of the precursor acetal, the cation concentration, or the method of production of cation (reaction with  $\text{SO}_4^{\bullet-}$  or photoionization). The lifetime of the cation does, however, decrease with increasing  $\text{pH}$  at  $\text{pH} > 9$ , which indicates that it reacts with  $\text{OH}^-$  (see section 4).

**c. Formation Mechanism of  $\text{Ph}\dot{\text{C}}\text{H}_2$  and the Carbocation.** The ESR, optical, and conductance results so far described can be explained in terms of formation of a radical cation followed by (a) heterolytic C–C fragmentation and, in competition, (b) hydration to give hydroxycyclohexadienyl radicals, as shown in eq 5. Deprotonation from  $\text{C}_\alpha$  (reaction c) is also a possibility (vide infra).



The reactivity of the radical cation shown in this scheme is analogous to that of radical cations from simpler benzene derivatives, such as  $\beta$ -phenylalkanols and ethers, as derived from ESR<sup>3,11</sup> and product analysis results.<sup>4,5,9,10,12</sup> The tendency of the radical cation to undergo C–C fragmentation is also very evident from the mass spectra, which are dominated by the presence of the ion  $\text{RC}^+(\text{OR}')_2$ , the molecular ion being essentially absent. An example for this is shown in Figure 5. In all cases the amplitude of the benzyl ion,  $\text{C}_6\text{H}_5\text{CH}_2^+$ , was much less than that of  $\text{RC}^+(\text{OR}')_2$ , evidence for the higher efficiency of the two oxygens, compared to phenyl, in stabilizing the positive charge.

In aqueous solution, there is obviously an alternative to C–C fragmentation and that is addition of a (nucleophilic) water molecule to the radical cation. This reaction (= hydration followed by deprotonation)<sup>3a</sup> leads to hydroxycyclohexadienyl radicals (eq 5b). In order to obtain an estimate of the ratio  $k(\text{heterolysis})$  (eq 5a) to  $k(\text{hydration})$  (eq 5b) for the case of  $\text{PhCH}_2\text{CH}(\text{OEt})_2$ , the experimental spectrum recorded after completion of the reaction with  $\text{SO}_4^{\bullet-}$  (at 800 ns; see Figure 2) was simulated by adding the pure spectrum of  $\text{Ph}\dot{\text{C}}\text{H}_2$  (from the reaction of  $\text{SO}_4^{\bullet-}$  with  $\text{PhCH}_2\text{CO}_2\text{H}$ )<sup>11</sup> to that of the  $\dot{\text{O}}\text{H}$  adduct (from reaction of pulse radiolytically produced  $\dot{\text{O}}\text{H}$ , yield  $\geq 90\%$ ), with different contributions of the two and taking account of the appropriate extinction coefficients. The best fit was obtained for a  $\sim 1:2$  rate ratio of the two competing reactions 5a:5b.

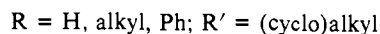
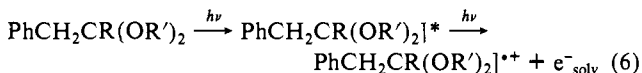
With radical cations of alkylated benzenes, deprotonation from  $\text{C}_\alpha$  is also a well-documented reaction.<sup>3-12,30</sup> The corresponding substituted benzyl radical (eq 5c) can be produced in a clean fashion by reaction with  $\text{O}^{\bullet-}$ , the latter obtained by deprotonation of  $\text{OH}^-$  produced by pulse radiolysis in 0.5 M NaOH solution.<sup>38</sup>

The spectrum of this radical (not shown) is somewhat similar to that of  $\text{Ph}\dot{\text{C}}\text{H}_2$ . The conclusion is then that deprotonation cannot be completely excluded, although by ESR only  $\text{Ph}\dot{\text{C}}\text{H}_2$ , the product of the C–C fragmentation reaction, was seen (see section 1a).

**2. Photoionization of Benzyl Acetals.** As already mentioned, benzyl radical and carbocation production can also be achieved in the absence of peroxydisulfate. As an example, in Figure 3 are shown absorption spectra observed on 248-nm laser photolysis of aqueous solutions at  $\text{pH} = 9$  containing only  $\text{PhCH}_2\text{CH}(\text{OEt})_2$  (saturated). The spectrum (a) recorded at 70 ns after the 20-ns pulse shows bands at 260, 305, and 315 nm, characteristic of  $\text{Ph}\dot{\text{C}}\text{H}_2$ , and a broad band with  $\lambda_{\text{max}} \geq 700$  nm. The latter can be made to disappear by adding typical hydrated electron scavengers such as  $\text{O}_2$ ,  $\text{N}_2\text{O}$ , or chlorinated hydrocarbons such as  $\text{CH}_2\text{Cl}_2$  or  $\text{HOCH}_2\text{CH}_2\text{Cl}$ . The remaining spectrum (b) (using  $\approx 50$  mM  $\text{CH}_2\text{Cl}_2$  to scavenge  $\text{e}^-_{\text{aq}}$ ) shows clearly the presence of  $\text{Ph}\dot{\text{C}}\text{H}_2$ , but there is also a broader band in the region 280–330 nm, similar to that formed on reaction with  $\text{SO}_4^{\bullet-}$  and assigned to the (isomeric) hydroxycyclohexadienyl radicals.

If the spectra of the radicals produced by direct photolysis are compared with those obtained by reaction with  $\text{SO}_4^{\bullet-}$  (Figure 2), it is evident that the spectra are very similar, which indicates that essentially the same products are formed in the two reactions. This means that the photochemistry with  $\lambda(\text{excitation}) = 248$  nm of  $\text{PhCH}_2\text{CH}(\text{OEt})_2$  in aqueous solutions consists essentially of ionization, i.e. there is little contribution of other photochemical reactions.<sup>39</sup> Photolysis with 248-nm light of this and related compounds is therefore a good entry into the radical cation chemistry of these molecules. The advantage of photoionization over oxidation with  $\text{SO}_4^{\bullet-}$  is that the former method provides the radical cation by a unimolecular process during the pulse, whereas the latter involves a bimolecular reaction whose rate depends on and is in practice limited by the concentration of the reactants. In cases where it is desired to produce species with a lifetime  $\leq 1$   $\mu\text{s}$  the photoionization route is to be preferred over that involving  $\text{SO}_4^{\bullet-}$ .

Concerning the mechanism of photoionization, the yields of  $\text{e}^-_{\text{aq}}$  (at  $\lambda = 600$  nm) and of  $\text{Ph}\dot{\text{C}}\text{H}_2$  (at 315 nm) were determined as a function of photon density in the range corresponding to 5–150 mJ/20-ns pulse, with an aqueous solution saturated with  $\text{PhCH}_2\text{CH}(\text{OEt})_2$  at  $\text{pH} \approx 9$ . The concentrations of both products increased linearly with the square of the laser intensity, which indicates that they are produced in a biphotonic process, eq 6,



followed by 5. This result is in agreement with expectation: On the basis of an ionization potential of 8.9 eV for  $\text{PhCH}_2\text{CH}(\text{OEt})_2$ ,<sup>40</sup> a 248-nm photon energy of 5 eV, and a hydration energy of the ions of  $\leq 3.5$  eV,<sup>41</sup> monophotonic ionization is thermodynamically not possible. The quantum yield of  $\text{e}^-_{\text{aq}}$  from eq 6,  $\text{R} = \text{H}$ ,  $\text{R}' = \text{Et}$ , was determined to be 0.07 at  $\sim 100$  mJ/pulse, with an aqueous solution of KI ( $\phi(\text{e}^-_{\text{aq}}) = 0.29$ ) as reference.

Results on the phenyl-substituted ketals (I,  $\text{R} = \text{Ph}$ ) have already been mentioned in the previous paragraph (see Figure 4). These compounds have the advantage of allowing one to detect and identify by optical methods not only the radical ( $\text{Ph}\dot{\text{C}}\text{H}_2$ ) but also the cation ( $\text{PhC}^+(\text{OR}')_2$ ) as the fragmentation products of the radical cation. The lifetimes of the ring-delocalized cations can thus be determined optically as well as by conductance.

With the use of the photoionization approach, an estimate can

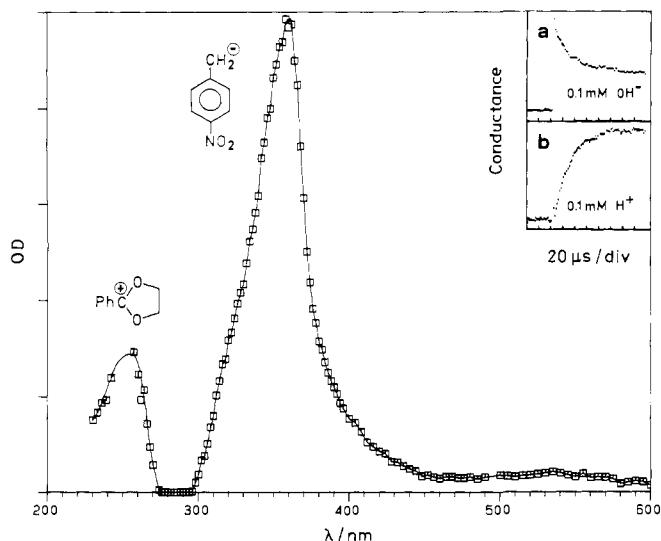
(37) (a) McClelland, R. A.; Ahmad, M. *J. Am. Chem. Soc.* **1977**, *99*, 5356. (b) *Ibid.* **1978**, *100*, 7031. (c) Ahmad, M.; Bergstrom, R. G.; Cashen, M. J.; Chiang, Y.; Kresge, A. J.; McClelland, R. A.; Powell, M. F. *Ibid.* **1979**, *101*, 2669. (d) McClelland, R. A.; Ahmad, M.; Bohonek, J.; Gedge, S. *Can. J. Chem.* **1979**, *57*, 1531.

(38) Neta, P.; Schuler, R. H. *Radiat. Res.* **1975**, *64*, 233.

(39) The same situation exists with respect to the photochemistry of other simple alkylated benzenes, e.g., benzyl alcohols,  $\beta$ -hydroxyphenylalkanes, and alkylbenzenes themselves (Ramaraj, R.; Steenken, S. Unpublished results; see also ref 41).

(40) From photoelectron spectroscopy using Ar (IP = 15.76 eV) for calibration. We thank B. Solouki, University of Frankfurt, for this measurement.

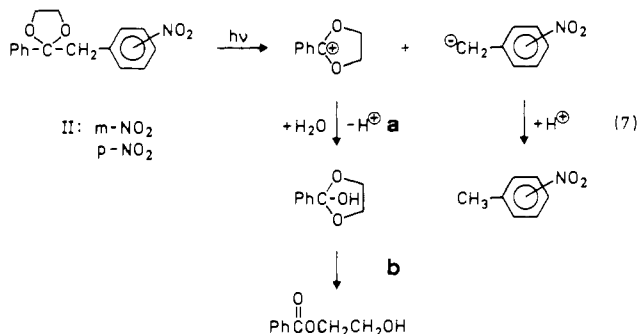
(41) Braun, M.; Fan, J. Y.; Fu, W.; Kompa, K. L.; Müller, G.; Schmid, W. E. In *Methods of Laser Spectroscopy*, Prior, Y., Ben-Reuven, A., Rosenbluh, M., Eds.; Plenum: London, 1986; p 367.



**Figure 6.** Absorption spectrum at 4–6  $\mu$ s following 248-nm photolysis of 2-(*p*-nitrobenzyl)-2-phenyl-1,3-dioxolane in argon-saturated 1:2 acetonitrile-water. The spectrum has not been corrected for depletion of parent which contributes a negative absorption at  $\sim$ 260 nm. The insets show traces obtained with conductivity detection in solutions containing 0.1 mM  $\text{OH}^-$  (a) and 0.1 mM  $\text{H}^+$  (b).

be made for the heterolysis rate constant  $k_{\text{het}}$  (see eq 5): Since there was no delay in the formation of  $\text{Ph}\dot{\text{C}}\text{H}_2$  (or of  $\text{PhC}^+(\text{OR})_2$ ) after the 10–20-ns laser pulse,  $k(\text{heterolysis})/\text{s} \geq \ln 2/1 \times 10^{-8} \approx 7 \times 10^7$ . For the radical cation of toluene (IP = 8.82 eV) in aqueous solution the rate constant for hydration (the dominant reaction) also is  $\geq 7 \times 10^7 \text{ s}^{-1}$ .<sup>42</sup> A similarly large number is expected for hydration of the radical cation of  $\text{PhCH}_2\text{CH}(\text{OEt})_2$ , on the basis of its IP of 8.9 eV. This means that the  $k(\text{heterolysis})$  values must also be  $\geq 7 \times 10^7 \text{ s}^{-1}$ , since C–C fragmentation competes with hydration efficiently.

**3. Photoheterolysis of Nitrobenzyl Acetals.** On the basis of product analysis, Wan has recently suggested that nitrobenzyl acetals II undergo C–C photoheterolysis producing carbocation and carbanion intermediates (eq 7).<sup>43</sup> The cation is identical with



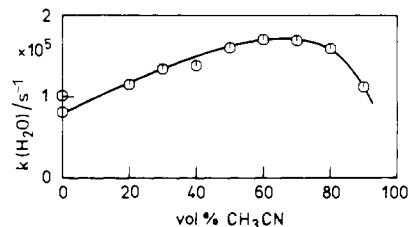
one formed by the radical cation route, and as a final check we have examined the two nitrobenzyl compounds. The absorption spectrum obtained with the para-substituted derivative has the 260-nm band characteristic of the 2-phenyl-1,3-dioxolan-2-ylum ion (Figure 6), with a second band centered at 355 nm. The latter decays very slowly ( $t_{1/2} > 1 \text{ s}$ ) and is identical with the band for the *p*-nitrobenzyl carbanion produced in the same solvent<sup>44</sup> by photodecarboxylation of the *p*-nitrophenylacetate ion.<sup>45</sup> Photolysis of the *m*-nitro compound resulted in the same band at 260 nm; however, the *m*-nitrobenzyl carbanion was not observed, from which it is concluded that it protonates within the 20-ns laser pulse.

(42) Steenken, S. J. Chem. Soc., Faraday Trans. 1 1987, 83, 113.

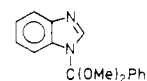
(43) Wan, P.; Muralidharan, S. Can. J. Chem. 1986, 64, 1949; J. Am. Chem. Soc. 1988, 110, 4336.

(44) Spectrum not shown. The absorption spectra of nitrobenzyl carbanions in aqueous acetonitrile are strongly solvent dependent; McClelland, R. A.; Steenken, S. Can. J. Chem. 1987, 65, 353.

(45) Margerum, J. D.; Petrusis, C. T. J. Am. Chem. Soc. 1969, 91, 2467.



**Figure 7.** The dependence on the water:acetonitrile ratio of the hydration rate constant  $k(\text{H}_2\text{O})$  of  $\text{PhC}(\text{OMe})_2^+$ , obtained by photoionization of  $\text{PhCH}_2\text{C}(\text{OMe})_2\text{Ph}$ . In pure  $\text{H}_2\text{O}$ , the cation precursor is



The spectrum recorded after the decay of the cation showed the 230-nm absorbance characteristic of the benzoate ester product (due to eq 7b). Experiments with conductivity detection were also carried out (see insets to Figure 6). Again there are characteristic increases in conductance in acid and decreases in basic solution (due to eq 7a) occurring with rates identical with those obtained optically at 260 nm. Moreover, these rates are the same, within experimental error, with the three precursors, the *m*- $\text{NO}_2$  and *p*- $\text{NO}_2$  acetals II and the acetal I with  $\text{R} = \text{Ph}$ ,  $\text{R}', \text{R}'' = -\text{CH}_2\text{CH}_2-$ . In other words the same cation is being produced with all three species.

**4. Lifetimes of Carbocations in Aqueous Solution.** With use of the methods described in sections 1–3 to produce cation and monitoring by conductance and, where possible, optically the reactions of the cations with water, the rate constants listed in Table I were obtained. For a number of ions are also given the rate constants obtained by the “stepwise hydride transfer” method.<sup>15,16</sup> As can be seen, the agreement between the values obtained by the two completely independent methods is very satisfactory. This supports strongly that one is dealing with the same cations and this is further support for the fragmentation pattern of the benzyl acetal radical cation as described by eq 5a.

Using the photoionization route to produce cation, two further reactivity parameters were investigated: (a) The influence of solvent composition (water:acetonitrile ratio) on the hydration rate constant  $k(\text{H}_2\text{O})$  of  $\text{PhC}^+(\text{OMe})_2$  is shown in Figure 7; there is a flat maximum between 50 and 70% acetonitrile. Similar trends have recently been seen with substituted di- and triphenyl carbenium ions.<sup>46</sup> (b) It was found that  $k(\text{obsd})$  for the decay of cation increased with increasing  $[\text{OH}^-]$  according to the relation  $k(\text{obsd}) = k(\text{H}_2\text{O}) + k(\text{OH}^-)[\text{OH}^-]$ . From these dependences the rate constants  $k(\text{OH}^-)$  for the reaction of cation with  $\text{OH}^-$  were obtained (see Table I). The value for  $\text{PhC}^+(\text{OMe})_2$  in water-acetonitrile 3:2 is  $7.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , and that for reaction with the more stable cation  $\text{PhC}^+(\text{OEt})_2$  is lower, i.e.  $2.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . A very interesting phenomenon is that the  $k(\text{OH}^-)$  value for  $\text{PhC}^+(\text{OMe})_2$  is smaller in pure water ( $2.8 \times 10^8$ ) than in water-acetonitrile 3:2 ( $7.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). This value is higher than the suggested<sup>47</sup> “limiting” value of  $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .

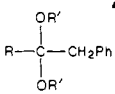








**5. Structure-Activity Relations for Addition of  $\text{H}_2\text{O}$  to  $\text{RC}^+(\text{OR}')_2$ , a.  $\text{R} = \text{H}$  or Alkyl.** As can be seen from Table I, replacement of two methoxyl groups by two ethoxyl groups or of these by isopropoxyl groups lowers the reactivity of the cations by roughly a factor of 10. This effect is independent of whether  $\text{R}$  is equal to H or alkyl (compare the couples 1/2, 3/4, 4/5). The dependence on  $\text{R}'$  of the rate constant corresponds to a Taft  $\rho^*$  value of  $\sim$ 4.4, the same as that recently found<sup>16</sup> for a larger number of di- and trialkoxycarbocations produced by stepwise hydride transfer.

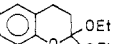
In that study<sup>16</sup> it was not possible to measure the hydration rate constants for cations with  $\text{R} = \text{H}$ , due to their too short lifetime. In the present work, however, this has been achieved. Their lifetime turns out to be longer than their formation period during

(46) McClelland, R. A.; Kanagathabapathy, V. M.; Banait, N.; Steenken, S. J. Am. Chem. Soc. 1989, 111, 3966.

(47) Richard, J. P.; Jencks, W. P. J. Am. Chem. Soc. 1984, 106, 1373.

Table I. Rate Constants for Addition of H<sub>2</sub>O to the Cations RC<sup>+</sup>(OR')<sub>2</sub> in Water or Water–Acetonitrile Mixtures at 20 ± 2 °C

no.	cation	$k(\text{H}_2\text{O})$ for cation precursor/s <sup>-1</sup>		$k(\text{OH}^- \text{ or } \text{N}_3^-)/\text{M}^{-1} \text{ s}^{-1}$
				
1	HC <sup>+</sup> (OEt) <sub>2</sub>	2 × 10 <sup>7</sup>	≥ 1 × 10 <sup>7</sup>	
2	HC <sup>+</sup> (OiPr) <sub>2</sub>	2.2 × 10 <sup>6</sup>		
3	MeC <sup>+</sup> (OMe) <sub>2</sub>	1.8 × 10 <sup>5</sup>	1.3 × 10 <sup>5</sup>	
4	MeC <sup>+</sup> (OEt) <sub>2</sub>	2.9 × 10 <sup>4</sup>	2.8 × 10 <sup>4</sup>	
5	MeC <sup>+</sup> (OiPr) <sub>2</sub>		2.0 × 10 <sup>3</sup>	
6	iPrC <sup>+</sup> (OMe) <sub>2</sub>	(7.8 ± 0.9) × 10 <sup>5</sup>	(7.6 ± 1) × 10 <sup>5</sup>	
7	R = Me	1.4 × 10 <sup>6</sup>	1.4 × 10 <sup>6</sup>	
8	R = Et	1.6 × 10 <sup>6</sup>		
9	R = nPr	1.3 × 10 <sup>6</sup>		
10	R = nBu	1.4 × 10 <sup>6</sup>		
11	R = iPr	1.8 × 10 <sup>6</sup>		
12	R = sBu	1.2 × 10 <sup>6</sup>		
13	R = tBu	1.5 × 10 <sup>6</sup>		
14		4.6 × 10 <sup>7</sup>		
15		3.8 × 10 <sup>4</sup>	3.5 × 10 <sup>4</sup>	
16		1.8 × 10 <sup>5</sup>	1.4 × 10 <sup>5</sup>	
17	PhC <sup>+</sup> (OMe) <sub>2</sub>	1.3 × 10 <sup>5</sup> <sup>c</sup>	1.2 × 10 <sup>5</sup> <sup>d</sup>	$k(\text{OH}^-) = 7.8 \times 10^8$ <sup>c</sup>
18	PhC <sup>+</sup> (OEt) <sub>2</sub>	4.3 × 10 <sup>4</sup>	(0.8–1) × 10 <sup>5</sup> <sup>e</sup>	$k(\text{OH}^-) = 2.8 \times 10^8$ <sup>e</sup>
19		4.0 × 10 <sup>4</sup>		$k(\text{OH}^-) = 2.0 \times 10^8$
20		3.8 × 10 <sup>4</sup> <sup>g</sup>		$k(\text{N}_3^-)_{\text{on}} = 1.4 \times 10^9$ <sup>f</sup>
21		8.6 × 10 <sup>2</sup>		$k(\text{N}_3^-)_{\text{off}} = 1.5 \times 10^5 \text{ s}^{-1}$ <sup>f</sup>
22	(MeO) <sub>3</sub> C <sup>+</sup>	5.2 × 10 <sup>3</sup> <sup>h</sup>	6.0 × 10 <sup>3</sup> <sup>h</sup>	
23	Ph <sub>3</sub> C <sup>+</sup>	1.5 × 10 <sup>5</sup> <sup>i</sup>	1.6 × 10 <sup>5</sup> <sup>k</sup>	
24		~ 1 × 10 <sup>5</sup> <sup>l</sup>		

<sup>a</sup>The water content is 50–80% (v/v). The rate constants are the average from values obtained in acid and basic solution, from conductance and, with the phenyl-substituted systems, from optical experiments. The error in the rate constants is estimated to be ±15%. <sup>b</sup>From ref 16. The solvent is water. <sup>c</sup>The solvent is W–AN 3:2. <sup>d</sup>From ref 37b. <sup>e</sup>The leaving group is benzimidazole; the solvent is 100% H<sub>2</sub>O. <sup>f</sup>From analysis of the biphasic decay of cation **19** in the presence of N<sub>3</sub><sup>-</sup>; for a description of the analysis in terms of  $k_{\text{on}}$  and  $k_{\text{off}}$  see ref 19a. <sup>g</sup>The leaving group is 4-O<sub>2</sub>NPhCH<sub>2</sub><sup>-</sup>. <sup>h</sup>Measured at [OH<sup>-</sup>] = 0.1 mM, the value is the sum of the  $k(\text{H}_2\text{O})$  and  $k(\text{OH}^-)$  values, cf. ref 15. <sup>i</sup>From ref 19. <sup>k</sup>The cation precursor is Ph<sub>3</sub>COPh. <sup>l</sup>The precursor is 

the 10–20-ns laser pulse. At pH 4–5 a first-order increase of conductance was seen which is assigned to the H<sup>+</sup> produced in the reaction of the cation with water. For the systems with R = H, the lowest rate constant measured is that for HC<sup>+</sup>(OiPr)<sub>2</sub> ( $k = 2.2 \times 10^6 \text{ s}^{-1}$ ). This rate is a factor 1100 larger than that<sup>16</sup> for MeC<sup>+</sup>(OiPr)<sub>2</sub> ( $k = 2.0 \times 10^3 \text{ s}^{-1}$ ). For HC<sup>+</sup>(OEt)<sub>2</sub>, the rate constant for reaction with H<sub>2</sub>O is  $2 \times 10^7 \text{ s}^{-1}$ , a factor ~10 larger than that for the isopropoxy derivative. For the couple HC<sup>+</sup>(OEt)<sub>2</sub>/MeC<sup>+</sup>(OEt)<sub>2</sub> the reactivity ratio is 1000, and for the cyclic cations H<sup>+</sup>COCMe<sub>2</sub>CM<sub>2</sub>EO/Me<sup>+</sup>COCMe<sub>2</sub>CM<sub>2</sub>EO it is 1200 (see Table I).

A pronounced increase in the stability of the cation on replacing H by Me is expected on the basis of the electron-donating and steric properties of Me as compared to H. However, what is unexpected is that the effect does not continue or is even inverted on going to the more electron-donating substituents Et to tBu (compare **7**–**13** or **3** with **6**). This “nonclassical” phenomenon has been seen before with a larger collection of cations and it has been explained in terms of (a) the Baker–Nathan effect, i.e. by the substituents' effects on solvation cancelling or even overcompensating their electronic and steric effects on “intrinsic” reactivity and (b) by steric inhibition of coplanarity (due to interaction between alkyl and alkoxy substituents in the preferred *Z,E*

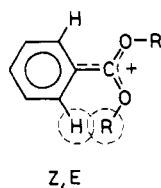
conformation of the acyclic ions).<sup>16</sup> The data presented in Table I are additional evidence for these phenomena in carbocation reactivity in aqueous solution.

**b. R = Phenyl.** As seen in Table I, MeC<sup>+</sup>(OMe)<sub>2</sub> (**3**) and PhC<sup>+</sup>(OMe)<sub>2</sub> (**17**) have about the same reactivity with H<sub>2</sub>O ( $k = (1.8 \text{ and } 1.2) \times 10^5 \text{ s}^{-1}$ ). From this it could, in principle, be concluded that Me and Ph stabilize dialkoxymethyl cations to the same extent.<sup>48</sup> However, this would be a wrong conclusion since with the (cyclic) 1,3-dioxolan-2-ylum cation Ph is much more stabilizing than Me (compare **19** ( $k = 4 \times 10^4 \text{ s}^{-1}$ ) with **7** ( $k = 1.4 \times 10^6 \text{ s}^{-1}$ )). The explanation for the apparent discrepancy involves steric inhibition of coplanarity in the case of the acyclic ion.  $\alpha$ -Dialkoxymethyl cations tend to adopt the *Z,E* conformation<sup>49</sup> in which the phenyl ortho hydrogens can interact with the alkyl groups, thus preventing full coplanarity and thereby

(48) It has in fact been argued on the basis of thermochemical considerations that the stabilizing effect on dialkoxymethyl cations is the same for Me and Ph (Larsen, J. W.; Bouis, P. A.; Riddle, C. A. *J. Org. Chem.* **1980**, *45*, 4969).

(49) Ramsey, B. G.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 3058. Paulsen, H.; Dammeyer, R. *Chem. Ber.* **1976**, *109*, 1837 and references therein. For a review, see: Perst, H. In *Carbocation Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1976; Vol. 5.

efficient charge delocalization. In contrast, there is no steric interaction possible when the alkoxy groups are held back as with



the cyclic systems **19–21**.<sup>50</sup> The phenyl group can then exert its full stabilizing influence by charge delocalization. In agreement with the idea of steric influence on coplanarity is the fact that with  $\text{PhC}^+(\text{OR})_2$  the stabilizing effect of replacing the methoxyl groups by ethoxyl groups corresponds to a factor of only 3 (compare **17** with **18**), whereas with  $\text{alkylC}^+(\text{OR})_2$  the average factor is  $\sim 10$ .<sup>16</sup>

It is interesting in this connection that the directly measured rate constant for hydration of the cation  $\text{PhC}^+(\text{OMe})_2$  ( $k = 1.3 \times 10^5 \text{ s}^{-1}$ ) is almost identical with that ( $1.2 \times 10^5 \text{ s}^{-1}$ )<sup>37b</sup> obtained by extrapolation to zero  $[\text{H}_2\text{SO}_4]$  of values measured in water– $\text{H}_2\text{SO}_4$  mixtures (see Table I).

It has previously been found that 2-alkyl-1,3-dioxan-2-ylum cations, which possess a 6-membered ring, are less reactive with water than the corresponding 5-membered systems, the 1,3-dioxolan-2-ylum cations.<sup>16</sup> The same difference is exhibited by the corresponding 2-phenyl derivatives, as seen by comparing **19** with **21** (Table I). The increased stability of the cation with the 6-membered ring is explainable<sup>16</sup> as resulting from the additional (electron-donating) methylene group compared with the 5-membered-ring cation. This effect overcompensates any opposite tendency resulting from more facile hybridization changes of the central carbon in the case of the 6-membered rings in going from the cation ( $\text{sp}^2$ ) to the hemioorthoester product ( $\text{sp}^3$ ).

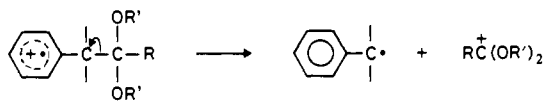
Comparison of the phenyl-substituted cations **19** and **20** shows that additional methyl groups at the alkoxy substituent lead to a pronounced increase of lifetime of the cation, analogous to the methyl-substituted cations **7** and **15**.<sup>16</sup>

The last entry in Table I refers to the bifunctional (distic)<sup>51</sup> radical/cation **24**. It is a tentative assignment for the  $\text{H}^+$ -generating species produced by photolysis of the cyclic ortho ester shown in the table.

## Summary and Conclusions

It has been shown that carbocations can be produced from benzyl acetals or ketals by one-electron oxidation using  $\text{SO}_4^{\cdot-}$  or by photoionization, which, in aqueous solution, proceeds in a biphotonic process. The radical cations thus formed, with the

positive charge and the unpaired spin presumably localized on the phenyl ring, undergo rapid hydration and equally, if not more, efficient C–C fragmentation to yield the benzyl radical and a dialkoxyethyl cation (half-life of the radical cation  $< 10\text{--}20$  ns). This C–C fragmentation (which leads to a separation of charge and spin) is formally a heterolytic process<sup>14,52</sup> of the E1 type



### C–C heterolysis

involving the transfer of the electron pair joining the dialkoxy substituted carbon with the benzyl carbon.<sup>53–55</sup> The driving force of this reaction (which mirror images the anion elimination reaction of benzyl halide or benzyl ether radical anions, eq 2) is obviously the electron pull exerted by the ionized phenyl ring,<sup>56</sup> plus the gain in solvation energy of the smaller as compared to the larger cation.

The carbocations produced in the fragmentation reactions have been identified by their absorption spectra or by their characteristic rates of reaction with water, as known from previous studies<sup>16</sup> using the stepwise hydride transfer technique. Several new cations (e.g., dialkoxyethyl cations  $\text{HC}^+(\text{OR})_2$ ) have been kinetically characterized, enabling known<sup>16</sup> structure–activity relations to be expanded. Other cations, such as the phenyl-substituted dialkoxyethyl cations  $\text{PhC}^+(\text{OR})_2$ , have been produced in aqueous solution and their reactivity has been directly studied for the first time. This information on structure–activity is of general relevance for a better understanding of  $\text{H}^+$  catalyzed solvolysis reactions such as acetal, ester and ortho ester hydrolysis, where  $\alpha$ -dialkoxyethyl cation-type intermediates are important.

(52) For a discussion of (terminology) problems in distinguishing between the concepts of homolysis and heterolysis in radical anion fragmentations, see ref 13c.

(53) In contrast, the elimination of  $\text{CH}_3^{\cdot}$  from the radical cation of 2-methyl-1,3-dioxolane observed at 77 K (Ushida, K.; Shida, T. *J. Am. Chem. Soc.* **1982**, *104*, 7332. Momose, T.; Tanimura, R.; Ushida, K.; Shida, T. *J. Phys. Chem.* **1987**, *91*, 5582) is a homolytic fragmentation.

(54) In the case of the "bibenzyl" acetals  $\text{PhCH}_2\text{C}(\text{OR})_2\text{Ph}$ , electron removal may lead to  $^{\cdot+}\text{PhCH}_2\text{C}(\text{OR})_2\text{Ph}$  ( $\text{A}^{\cdot+}$ ) or to  $\text{PhCH}_2\text{C}(\text{OR})_2\text{Ph}^{\cdot+}$  ( $\text{B}^{\cdot+}$ ). Since  $-\text{C}(\text{OR})_2$  is an electron-withdrawing substituent,  $\text{A}^{\cdot+}$  will be more stable than  $\text{B}^{\cdot+}$ . The intramolecular electron transfer reaction  $\text{B}^{\cdot+} \rightarrow \text{A}^{\cdot+}$  is thus expected to be exothermic. Intramolecular electron transfer can be very rapid (Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047. Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*. Miller, J. R. *Nouv. J. Chim.* **1987**, *11*, 83).

(55) If C–C fragmentation was taking place from  $\text{B}^{\cdot+}$  (see ref 54), this would constitute a homolytic reaction.

(56) For the model compound  $\text{PhCH}_2\text{CH}_2\text{OH}$ , it can be calculated by a thermochemical cycle using BDE ( $\text{PhCH}_2\text{CH}_2\text{OH}$ ) = 70 kcal mol<sup>-1</sup>, IP ( $\text{PhCH}_2\text{CH}_2\text{OH}$ ) = 8.9 eV, and IP ( $\text{CH}_2\text{OH}$ ) = 7.6 eV that BDE ( $\text{PhCH}_2\text{CH}_2\text{OH}^{\cdot+} \rightarrow \text{PhCH}_2^{\cdot} + \text{CH}_2\text{OH}^+$ ) = 40 kcal mol<sup>-1</sup>, which shows the pronounced weakening of the "scissile" bond. For the benzyl acetal radical cations the bond will be even more weakened, due to the lower IP of the  $\alpha$ -dialkoxyethyl radicals as compared to  $\text{CH}_2\text{OH}$ .

(50) This type of explanation for analogous phenomena has previously been given by Chiang et al.: Chiang, Y.; Kresge, A. J.; Salomaa, P.; Young, C. I. *J. Am. Chem. Soc.* **1974**, *96*, 4494.

(51) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805.