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Radiation Chemical Production and Lifetimes of Trialkoxymethyl Carbocations in Aqueous Solution

S. Steenken,*[1] J. Buschek, and R. A. McClelland[2]

Contribution from the Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim, West Germany.

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Abstract: Trialkoxymethyl radicals were produced in aqueous solution by H abstraction from trialkoxymethanes by OH and H. The radicals were then oxidized by one-electron transfer to give trialkoxymethyl carbocations. The reactions of the cations with water and with OH^- were studied by using time-resolved conductance techniques. $(CH_3O)_3C^+$ hydrolyzes with a rate constant of $(1.4 \pm 0.2) \times 10^3\ s^{-1}$ and it reacts with OH^- with $k = (7 \pm 1) \times 10^7\ M^{-1}\ s^{-1}$. The activation parameters for the reaction with water are $E_A = 7.6$ kcal/mol and $\Delta S^{\ddagger} = -20.2$ eu. Replacement of methoxy in the cation by ethoxy and isopropoxy leads to a pronounced decrease in the rate constants for these processes: the Taft ρ^* values for reaction of $(RO)_3C^+$ with H_2O and OH^- are 5.7 and 3.7, respectively. With cyclic trialkoxymethyl cations that from the six-membered 1,3-dioxane system is more stable than that from 1,3-dioxolane, the five-atom counterpart. Trialkoxymethyl cations are also produced by a β-fragmentation reaction from α-(β-trialkoxy)methoxyalkyl cations.

α-Hydroxyalkyl and α-alkoxyalkyl radicals can be conveniently produced by H abstraction from alcohols, ethers, and acetals. These radicals have long been known to be oxidizable by a variety of organic and inorganic oxidants.[3-6] If, as assumed,[6] the oxidation reactions proceed by one-electron transfer, the radicals are converted into carbocations by the oxidation process. Generation of a radical by H abstraction from a molecule followed by one-electron oxidation of the radical therefore constitutes a general method of carbocation production equivalent to abstracting a hydride ion from the precursor molecule. If radical production and its oxidation can be made to occur in periods shorter than the carbocation lifetime, the physical and kinetic properties of the carbocation can be studied.[7,8] This approach has previously been taken to generate simple (not substituted by heteroatoms) aliphatic carbocations;[9] however, their lifetime was too short to permit their study. In the present paper the method of carbocation formation by consecutive removal of electrons (plus a proton) is applied to the other extreme, i.e., to systems that are multiply stabilized by heteroatoms at C_α:

$$(RO)_3CH \xrightarrow{-H^\cdot} (RO)_3\dot{C} \xrightarrow{-e^-} (RO)_3C^+$$

Trialkoxy carbocations were first prepared and isolated by Meerwein and co-workers,[10,11] and their physical properties have been studied in nonaqueous solution.[12] Recently, estimates of the lifetimes of various mono-, di-, and trialkoxy carbocations in aqueous solution have been reported.[13,14] However, no direct measurement of such lifetimes in water seems to have been carried out. We report here the first direct measurement of the rates of reaction of trialkoxy carbocations in aqueous solution. These rates are of interest due to the role of alkoxy carbocations in the acid-catalyzed hydrolysis of acetals, ketals, and ortho esters.[14-17] Evidence is also presented for a novel unimolecular fragmentation reaction of monoalkoxy carbocations.

Experimental Section

Acyclic ortho esters were commercially available. They were purified (to a purity ≥99% (GC)) by fractional distillation and stored in sealed ampules under Ar. 2-Methoxy(or isopropoxy)dioxolane and 2-methoxy-1,3-dioxane were prepared by ortho ester exchange of trimethyl(or isopropyl) orthoformate and 1 equiv of the appropriate diol. Sodium hexachloroiridate (IV), potassium hexacyanoferrate (III), and tetranitromethane were of the highest purity commercially available and were used as received.

The triethoxymethyl carbocation was prepared as its BF_4^- salt by treatment of tetraethyl orthocarbonate with BF_3 etherate, following standard procedures.[10,13] The 2-methoxy-1,3-dioxolan-2-ylium cation was prepared as a solution in 96% H_2SO_4 by careful addition of 2,2-dimethoxy-1,3-dioxolane. The latter compound was prepared by the ortho ester interchange reaction of tetramethyl orthocarbonate and 1 equiv of ethylene glycol. First-order rate constants for the hydrolysis of the two cations were determined in aqueous H_2SO_4, 68–75% H_2SO_4 for $(CH_3CH_2O)_3C^+$ and 83–90% H_2SO_4 for 2-methoxy-1,3-dioxolan-2-ylium cation, following changes in the NMR spectra.

Pulse radiolysis was performed on solutions prepared with reagent grade water from a Millipore Milli-Q system. The solutions were saturated with N_2O to convert e_{aq}^- into OH, and they were then irradiated with 0.1- to 1-μs pulses from a 3 MeV van de Graaff accelerator with dose rates of 300 rads per pulse, thus producing initial radical concentrations of $\approx 2\ \mu M$. Substrate concentrations were 5–50 mM, oxidant concentrations were 0.08–1 mM, and the pH was varied from 7 to 12 with barium hydroxide. Experiments to obtain rates in nonalkaline solutions were carried out between pH 6.5 and 5.5, the pH being adjusted with $HClO_4$.

Production and decay of the alkoxyalkyl carbocations was monitored by observing changes in the conductance of the solutions. Conductance experiments were carried out with a 10 MHz AC or a DC method. The signals were fed into a Biomation 8100 transient recorder interfaced with a VAX 11/38 computer via a PDP 11/10. The digitized data were stored and analyzed with the VAX. The data were referenced to three dosimetry systems: (a) a solution at pH 4–5 containing 0.1 M *tert*-butyl alcohol and saturated with CH_3Cl for which $G(HCl) = 3.14$;[18] (b) a N_2O

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[1] This author dedicates the paper to Prof. G. Wilke on the occasion of his 60th birthday.

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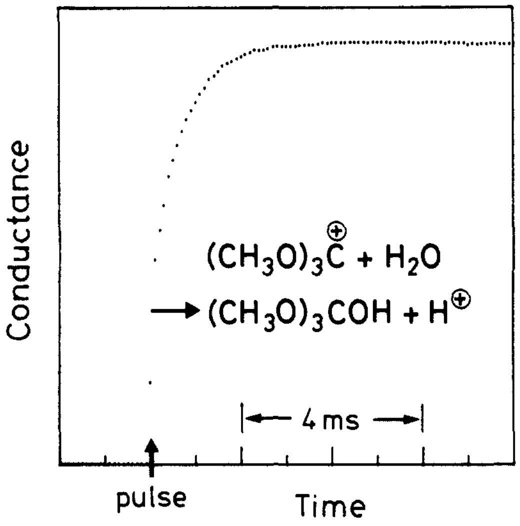

Figure 1. Conductance change observed on producing $(CH_3O)_2CHO\dot{C}H_2$ and $(CH_3O)_3\dot{C}$ in the presence of 0.5 mM $Fe(CN)_6^{3-}$ at pH 6.2. $[(CH_3O)_3CH]$ = 10 mM.

saturated solution at pH ≈5 that contained 10 mM dimethyl sulfoxide for which, as compared to solution a, $G(H^+) = G(CH_3SO_2^-)$[19] was found to be 6.0; and (c) a N_2O saturated solution at pH 5–6 containing 0.1 M methanol and 0.5 mM oxidant (Ox) for which $G(H^+) = G(Ox^{\bullet -}) = G(OH + H) = 6.6$. By comparing the amplitudes of the signals from system c with those from system b and taking 315 and 35 cm^2 ohm^{-1} mol^{-1} for the ion mobilities of H^+ and $CH_3SO_2^-$, respectively, the *difference* in the ion mobilities between $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ and that between $IrCl_6^{4-}$ and $IrCl_6^{3-}$ was determined to be 10 and 100 cm^2 ohm^{-1} mol^{-1}, respectively. These numbers have been used to calculate from the measured conductance changes the equivalents of H^+ produced per equivalent of radical.

Results and Discussion

(1) Trimethoxymethane. Figure 1 shows the buildup of the conductance of an aqueous solution containing 10 mM trimethoxymethane (trimethyl orthoformate) and 0.5 mM $Fe(CN)_6^{3-}$ at pH 6.2 after producing ≈2 μM OH (90%) + H (10%) by a 0.4-μs electron pulse. On the basis of the calibration the overall conductance change is primarily due to production of 1 equiv of H^+. It is evident that there are two components: a fast one that accounts for approximately 50% of the total conductance increase, and a slow component that yields the remaining 50%. The rate of the fast component was found to increase with increasing concentration of $Fe(CN)_6^{3-}$ (measured from 0.02 to 0.4 mM) and from this linear dependence the rate constant for production of conductance by reaction of $Fe(CN)_6^{3-}$ with the radical $(CH_3O)_2CHO\dot{C}H_2$ (eq 6, see below) was obtained as 1.8×10^9 M^{-1} s^{-1}. In contrast to the fast component, the rate of conductance increase via the *slow* component was found to be *in*dependent of $[Fe(CN)_6^{3-}]$ in the range 0.1–2 mM. The rate constant measured for this process at pH 6–6.5 is $(1.4 \pm 0.1) \times 10^3$ s^{-1}. After completion of the slow reaction, the total yield of the conductance change was equal within ±2% to that from the reaction of $\dot{C}H_2OH$ with $Fe(CN)_6^{3-}$ in which H^+ is quantitatively produced (Experimental Section).

When ferricyanide was replaced as the oxidant by hexachloroiridate (IV), a two-step formation of conductance was again seen. As with ferricyanide, the rate of the fast step was dependent on $[IrCl_6^{2-}]$ (between 0.02 and 0.1 mM), whereas that of the slow component was not (between 0.1 and 1 mM). From the dependence on $[IrCl_6^{2-}]$ of the fast conductance increase the rate constant for production of conductance by reaction of $IrCl_6^{2-}$ with $(CH_3O)_2CHO\dot{C}H_2$ was found to be 3.8×10^9 M^{-1} s^{-1}. The rate constant for the slow process was measured to be 1.4×10^3 s^{-1}, i.e., equal to that found when ferricyanide was the oxidant.

The results described are explained by eq 1–8. Equation 1

$$H_2O \rightarrow H^+, OH, H, e_{aq}^-, OH^- \qquad (1)$$

whereby $[H^+] = [e_{aq}^-] + [OH^-]$

$$e_{aq}^- + N_2O + H_2O \rightarrow OH^- + OH + N_2 \qquad (2)$$

$$H^+ + OH^- \rightarrow H_2O \qquad (3)$$

$$(CH_3O)_3CH + OH(H) \xrightarrow{a} \underset{I}{(CH_3O)_3\dot{C}} + H_2O(H_2)$$
$$\xrightarrow{b} \underset{II}{(CH_3O)_2CHO\dot{C}H_2} + H_2O(H_2) \qquad (4)$$

$$(CH_3O)_3C + Ox \rightarrow \underset{I^+}{(CH_3O)_3C^+} + Ox^{\bullet -} \qquad (5)$$

$$(CH_3O)_2CHO\dot{C}H_2 + Ox \rightarrow \underset{II^+}{(CH_3)_2CHOC^+H_2} + Ox^{\bullet -} \qquad (6)$$

$$(CH_3O)_3C^+ + H_2O \rightarrow (CH_3O)_3COH + H^+ \qquad (7)$$

$$(CH_3O)_2CHOC^+H_2 + H_2O \rightarrow (CH_3O)_2CHOCH_2OH + H^+ \qquad (8)$$

$$(CH_3O)_3C^+ + OH^- \rightarrow (CH_3O)_3COH \qquad (9)$$

identifies the radicals and ions produced in the radiolysis of water; after completion of reaction 2 (half-life < 5 ns), $[H^+] = [OH^-]$. The rate of the neutralization reaction, eq 3, depends on pH: at pH 6 its half-life is ≈5 μs, which means that at pH 6 only processes with reaction periods longer than ≈5 μs can be kinetically studied by the conductance technique. In eq 4 it is shown that OH (and H) react with $(CH_3O)_3CH$ by H abstraction from the central and from the external carbons. The radicals I and II are produced with equal yields. This is deduced from the experimentally observed ratio of the fast and the slow component expressed in terms of equivalents of H^+.

Taking into account the difference in number of hydrogen atoms in the two groups the 1 to 1 ratio translates into a 9:1 preference for abstraction of the central hydrogen. This type of selectivity for H-abstraction reactions of OH (and possibly H) is in agreement with earlier data[5] relating to ethers and acetals.

Both radicals formed in eq 4 are oxidized to give the carbocations I^+ and II^+ (eq 5 and 6). The monoalkoxylated cation II^+ reacts rapidly with water to give H^+ and a hemiacetal. This process (eq 8) is responsible for the fast rise of conductance. Since the rate of this fast component is dependent on the oxidant concentration, the hydration of the monoalkoxylated carbocation is obviously not rate determining. Since, due to the neutralization reaction, at pH 6 rates larger than $\approx 1 \times 10^5$ s^{-1} cannot be measured, this value can be identified as the lower limit for the rate of reaction 8.

In order to get a more precise estimate of the lifetime in water of a monoalkoxy carbocation, the 2-isopropoxypropan-2-yl radical was produced at pH 4 by H abstraction from ≈0.18 M diisopropyl ether in the presence of $IrCl_6^{2-}$, and the conductance of the solution was monitored. The reaction between $(CH_3)_2CHO\dot{C}(CH_3)_2$ and $IrCl_6^{2-}$ proceeds by one-electron transfer with $k = 3.6 \times 10^9$ M^{-1} s^{-1}.[9] It was found to yield 1 equiv of H^+ per $(CH_3)_2CHO\dot{C}(CH_3)_2$. The rate of H^+ production by hydrolysis of the 2-isopropoxypropan-2-ylium carbocation increased linearly with increasing $[IrCl_6^{2-}]$ up to 2 mM, where the rate of oxidation of $(CH_3)_2CHO\dot{C}(CH_3)_2$ is equal to $(3.6 \times 10^9)(2 \times 10^{-3})$ s^{-1} = 7.2×10^6 s^{-1}. The rate constant for hydrolysis of the carbocation must therefore be larger than this number. Taking into account the experimental error limits and signal-to-noise, the rate constant is estimated to be $\geq 2 \times 10^7$ s^{-1}.

The oxidation of the organic radicals (eq 5 and 6) can also be studied by observing the corresponding reduction in the concentration of the oxidant. In the case of ferricyanide its bleaching was monitored at λ = 420 nm with solutions buffered to pH ≈8 with ≤1 mM phosphate.[20] There appeared to be only one com-

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ponent in the bleaching at 420 nm, with the *yield* of ferricyanide consumption being equal to that of the initial yield of OH + H. This means that the radicals I and II react with ferricyanide with the same rate constant ($k(5) \approx k(6)$, determined to be 1.7×10^9 M^{-1} s^{-1}, i.e., essentially equal to $k(6)$ as obtained from the conductance experiments).

When $IrCl_6^{2-}$ was used as the oxidant instead of ferricyanide, also only one kinetic component in its depletion (monitored at λ = 490 nm) was seen. The *amount* of bleaching was equal to that found when $\dot{C}H_2OH$ was used to reduce $IrCl_6^{2-}$ (=100%). As with ferricyanide, it can therefore be concluded that with $IrCl_6^{2-}$ the rate constants for reactions 5 and 6 are the same, which means that $IrCl_6^{2-}$, like $Fe(CN)_6^{3-}$, does not differentiate kinetically between the strong reductant $(CH_3O)_3\dot{C}$ and the weaker electron-donor $(CH_3O)_2CHO\dot{C}H_2$. The rate constants for reaction 5 and 6 with Ox = $IrCl_6^{2-}$ were determined as 3.8×10^9 M^{-1} s^{-1}, similar to those of other[9] α-alkoxyalkyl radicals and in agreement with the value for $k(6)$ from conductance.

As a third oxidant, tetranitromethane (TNM) was used. Its redox potential is not known, due to lack of reversibility in the one-electron reduction. However, TNM has been found an efficient yet selective oxidant for a variety of organic radicals.[4,5,21,22] When radicals I and II were produced in the presence of 0.1–1 mM TNM at pH 7.9, the formation of the nitroform anion (monitored at λ = 350 nm) was observed. It occurred in two steps: a fast one (half-lifes ≤10 μs) the rate of which depended on the TNM concentration and whose yield was ≈50% of that of OH + H, and a slow one (half-life 184 μs), which accounted for the remaining 50% and whose rate was *in*dependent of the TNM concentration. The fast process is assigned to reaction of $(CH_3O)_3\dot{C}$ with TNM by one-electron transfer (eq 10) with a

$$(CH_3O)_3\dot{C} + (NO_2)_4C \xrightarrow{k} (CH_3O)_3C^+ + NO_2\cdot + C(NO_2)_3^- \quad (10)$$

measured k of $\approx 2 \times 10^9$ M^{-1} s^{-1}, whereas the slow, unimolecular formation of $C(NO_2)_3^-$ is suggested to be due to heterolytic decomposition of the nitroxide formed by addition of radical II to TNM, cf. reactions 11 and 12, followed by rapid hydrolysis of II^+. Oxidation by TNM of α-monoalkoxyalkyl radicals via an

$$(CH_3O)_2CHO\dot{C}H_2 + C(NO_2)_4 \rightarrow \underset{\text{ad}}{(CH_3O)_2CHOCH_2ON(O\cdot)C(NO_2)_3} \quad (11)$$

$$\text{ad} \rightarrow \underset{II^+}{(CH_3O)_2CHOC^+H_2} + NO_2\cdot + C(NO_2)_3^- \quad (12)$$

addition/elimination sequence as with eq 11/12 is well documented.[5]

The optical results with TNM thus confirm the findings from conductance obtained with the stronger oxidants, i.e., that radicals I and II are produced in about equal yields. For the purpose of studying the hydrolysis of I^+, TNM is not a good oxidizing system, since the heterolysis of the nitroxide (eq 12) occurs on a similar time scale.

Conductance experiments were carried out also in basic solution (pH 9–11). Under these conditions the H^+ produced by hydrolysis of the carbocations (eq 7 and 8) is removed by the excess OH^- present. This leads to a decrease of conductance. Due to the difference in lifetime of the cations I^+ and II^+, the conductance decrease occurs in two steps. It was found that the rate of the slow step increased with increasing $[OH^-]$ according to the equation $k_{obsd} = k(H_2O) + k(OH^-)[OH^-]$. This is explained in terms of reaction of I^+ with OH^-, cf. eq 9. From the above dependence the bimolecular rate constant for reaction 9 was obtained as $(5.7 \pm 0.4) \times 10^7$ M^{-1} s^{-1}. The intercept of the k_{obsd} vs. $[OH^-]$ plots represents the "spontaneous" hydrolysis of I^+ ($k = (1.4 \pm 0.3) \times 10^3$ s^{-1}) and should therefore be equal to the rate measured in acid solution. This is, in fact, the case, as shown in Table II.

Table I. Rate Constants for Reaction of $IrCl_6^{2-}$, $Fe(CN)_6^{3-}$, and $C(NO_2)_4$ with Radicals Derived from Orthoformates and Orthocarbonates[a]

radical	k/M^{-1} s^{-1}		
	$IrCl_6^{2-}$ [b]	$Fe(CN)_6^{3-}$ [c]	$C(NO_2)_4$ [d]
$(CH_3O)_3\dot{C}$ (I)	3.8×10^9	1.7×10^9	$\approx 2 \times 10^9$
$(CH_3O)_2CHO\dot{C}H_2$ (II)	3.8×10^9	1.7×10^9	$\approx 1 \times 10^9$ [f]
	3.8×10^9 [e]	1.8×10^9 [e]	
$(C_2H_5O)_3\dot{C}$ (III)	2.9×10^9	1.6×10^9	
$(C_2H_5O)_2CHO\dot{C}HCH_3$ (IV)	2.9×10^9	1.6×10^9	
	2.8×10^9 [e]		
$((CH_3)_2CHO)_3\dot{C}$ (VI)	2.8×10^9	2.7×10^9	
$((CH_3)_2CHO)_2CHO\dot{C}(CH_3)_2$ (VII)	2.8×10^9	2.7×10^9	
$(CH_3O)_3CO\dot{C}H_2$ (XII)	3.0×10^9	3.8×10^8	
	4.0×10^9 [e]		
$(C_2H_5O)_3CO\dot{C}HCH_3$ (XIII)	2.2×10^9	1.8×10^9	
	3.4×10^9 [e]		

[a] [Substrate] ≈ 10 mM, [oxidant] = 0.05–0.5 mM, 20 °C. [b] From optical experiments at λ = 490 nm and pH 7–8. [c] From optical experiments at λ = 420 nm and pH 7–8. [d] From optical experiments at λ = 350 nm and pH 7.9. [e] From conductance experiments. [f] Measured at λ = 300 nm.

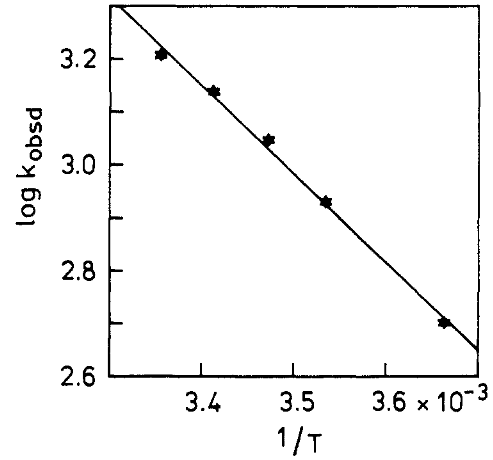
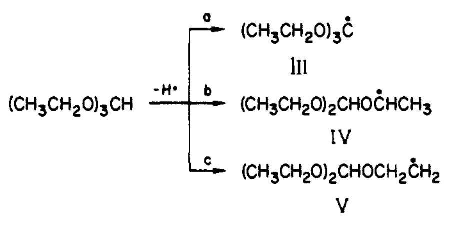


Figure 2. Arrhenius plot of the rate data for hydrolysis of $(CH_3O)_3C^+$: 10 mM $(CH_3O)_3CH$, 0.5 mM $K_3Fe(CN)_6$, pH 6.2.

Studies were also carried out by varying the oxidant concentration at a fixed pH. No change in rate was observed for the slow step, while an increase in rate was seen for the fast step, thus confirming the observation in acid solution that the oxidation of II is rate determining and not the hydrolysis of the corresponding carbocation II^+. This result also shows that the change in rate due to changing $[OH^-]$ is not an effect of varying the ionic strength of the solution.

The Activation Parameters for the Hydrolysis of $(CH_3O)_3C^+$. These were determined by using a solution of 10 mM trimethoxymethane and 0.5 mM ferricyanide at pH 6.2 and varying the temperature between 0 and 25 °C. From the Arrhenius plot of the rate data (Figure 2; correlation coefficient 0.998), $E_A = (7.6 \pm 1.3)$ kcal/mol, $\Delta S^\ddagger = -(20.2 \pm 4.4)$ cal mol^{-1} K^{-1}, and $A = 6.4 \times 10^8$ s^{-1}.

(2) Triethoxymethane. From this compound *three* different radicals can be produced by H abstraction: The α-alkoxyl-



(13)

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[20] With this oxidant there is a spectral "window" between ≈230 and ≈280 nm. In this region small absorbance changes were seen after the electron pulse. However, it is not clear whether these can be assigned to the cation I^+. Taft (ref 12) states that no spectral transition with $\epsilon > 10$ M^{-1} cm^{-1} can be found above 190 nm for $(C_2H_5O)_3C^+$ in acetonitrile.

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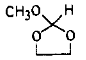
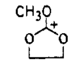
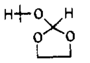
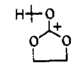
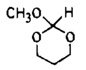
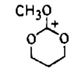
[22] Hazra, D. K.; Steenken, S. *J. Am. Chem. Soc.* **1983**, *105*, 4380.

Table II. Rate Constants for Reaction of α-Alkoxymethyl Carbocations in Aqueous Solution[a]

parent compd	cation	$k(H_2O)/s^{-1}$	$k(H_2O)^b/s^{-1}$	$k(OH^-)^c/M^{-1}\ s^{-1}$
$((CH_3)_2CH)_2O$	$(CH_3)_2CHOC^+(CH_3)_2$	$>2 \times 10^7$		
$(CH_3O)_3CH$	$(CH_3O)_3C^+$ (I^+)	$(1.4 \pm 0.3) \times 10^{3\,d}$ $(1.4 \pm 0.1) \times 10^{3\,e}$	$5 \times 10^{2\,f}$	$(5.7 \pm 0.4) \times 10^7$
$(CH_3O)_4C$	$(CH_3O)_3C^+$ (I^+)	$(1.5 \pm 0.2) \times 10^{3\,d}$ $(1.4 \pm 0.2) \times 10^{3\,e}$		$(8.6 \pm 0.6) \times 10^7$
$(C_2H_5O)_3CH$	$(C_2H_5O)_3C^+$ (III^+)	59 ± 9^d 67 ± 6^e	20	$(9.6 \pm 1.0) \times 10^6$
$(C_2H_5O)_4C$	$(C_2H_5O)_3C^+$ (III^+)	62 ± 4^e		
$((CH_3)_2CHO)_3CH$	$((CH_3)_2CHO)_3C^+$ (VI^+)	$1^{d,g}$		$(3.6 \pm 0.4) \times 10^5$
	 (IX^+)	$(2.7 \pm 0.3) \times 10^{4\,d}$	1.1×10^5	$(2.8 \pm 0.3) \times 10^8$
	 (X^+)	$(5.3 \pm 0.5) \times 10^{3\,d}$ $(4.9 \pm 0.5) \times 10^{3\,e}$		$(2.8 \pm 0.2) \times 10^7$
	 (XI^+)	$(5.4 \pm 1.1) \times 10^{3\,d}$ $(3.8 \pm 0.1) \times 10^{3\,e}$		$(7.9 \pm 0.5) \times 10^7$

[a] At 20 ± 2 °C and ionic strengths between 0.2 and 10 mM. [b] Estimated by extrapolation from aqueous H_2SO_4. [c] From the slope of k(obsd) vs. $[OH^-]$ plots. [d] From the intercept of k(obsd) vs. $[OH^-]$ plots. [e] From measurements at pH 6–6.5. [f] From ref 13. [g] The rate constant may be in the range (1–5) s^{-1}. 1 s^{-1} is the most probable number.

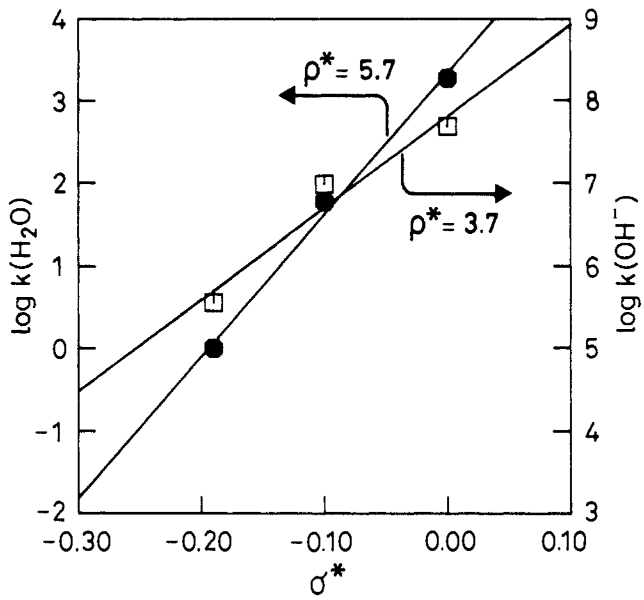


Figure 3. The dependence of log $k(H_2O)$ (circles) and log $k(OH^-)$ (squares) on the σ^* values of the substituents methyl, ethyl, and isopropyl. By taking into account that there are *three* substituents at C_α, the slopes correspond to Taft ρ^* values of 5.7 and 3.7, respectively.

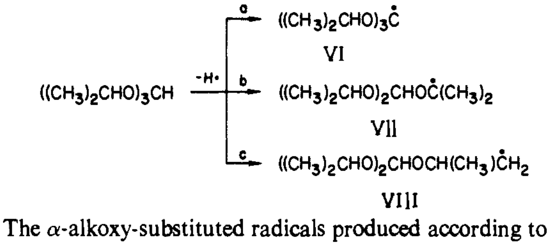
substituted radicals formed according to eq 13a and 13b should be good one-electron donors in contrast to the β-substituted radical produced in eq 13c. When these radicals were generated in the presence of 0.05–0.5 mM $IrCl_6^{2-}$ at pH ≈8, a bleaching of the absorption at 490 nm was observed that corresponded to the full yield of OH + H. Thus all three radicals formed in eq 13 react with $IrCl_6^{2-}$ ($k = 2.9 \times 10^9\ M^{-1}\ s^{-1}$, Table I). With the same solutions at pH 9.5–11, but using conductance detection, a two-step decrease of conductance was seen, i.e., via a fast component, whose rate depended on $[IrCl_6^{2-}]$, and a very slow one, the rate of which was *in*dependent of $[IrCl_6^{2-}]$.

The results are explained by assuming that III and IV are oxidized by one-electron transfer to give the corresponding carbocations. That from IV is rapidly hydrated to yield H^+. Since this reaction is very fast ($k > 2 \times 10^7\ s^{-1}$) it is the *oxidation* of IV which is rate limiting (studied up to 0.5 mM $IrCl_6^{2-}$). The reaction with H_2O of the triethoxymethane carbocation produced from III generates the slow conductance change. In this case, as with the trimethoxymethyl radical, the oxidation step is much faster than the hydrolysis of the resulting carbocation.

The oxidant $Fe(CN)_6^{3-}$ was also used. In experiments at pH 8–9 and with optical detection, only one kinetic component was recognizable in the bleaching at λ = 420 nm, indicating that III and IV reduce ferricyanide with equal rates (see Table I). With solutions containing up to 1 mM ferricyanide, the amount of its depletion at 100 μs after initiation of the reaction corresponded to only 93% of the full radical yield. This is as expected if V reacts with ferricyanide with a rate constant $k < 10^7\ M^{-1}\ s^{-1}$, a reasonable[9] value for an alkyl radical not substituted at C_α by a heteroatom.

Experiments were also performed in basic solution by monitoring the conductance. Similar to the trimethoxymethane system, a fast and a slow component in the reduction of the conductance of the solution were observed. The rate of the slow step, while being *in*dependent of the concentration of oxidant, was found to depend on $[OH^-]$ according to the equation $k_{obsd} = k(H_2O) + k(OH^-)[OH^-]$. From this dependence the $k(H_2O)$ and $k(OH^-)$ values for the reaction of $(C_2H_5O)_3C^+$ (III^+) with H_2O and OH^- were obtained as 59 s^{-1} and $9.6 \times 10^6\ M^{-1}\ s^{-1}$, respectively (Table II). In acid solution (pH ≈6.5) the hydrolysis of III^+ results in an *in*crease of conductance. The rate constant $k(H_2O)$ measured is 67 s^{-1}, in good agreement with the value from the k_{obsd} vs. $[OH^-]$ plot.

(3) Triisopropoxymethane. Three different radicals can be generated from this compound by H abstraction:



(14)

The α-alkoxy-substituted radicals produced according to eq 14a and 14b are expected to react with $IrCl_6^{2-}$ and $Fe(CN)_6^{3-}$ by electron transfer to give the corresponding cations VI^+ and VII^+, whereas radical VIII should not yield the cation.[9] The results of conductance experiments at pH 9–11 are in agreement with this expectation: there was a fast conductance change whose rate was dependent on oxidant concentration and a very slow additional conductance change whose rate was invariant with [oxidant]. The fast change is assigned to hydrolysis of VII^+ and the slow one to that of VI^+.

As in the previous cases, the rate constant for reaction of $((CH_3)_2CHO)_3C^+$ with OH^- was determined by measuring the increase in the (slow) rate of conductance decrease between pH 9 and 11. A value of $3.6 \times 10^5\ M^{-1}\ s^{-1}$ was obtained for $k(OH^-)$, and, from the intercept, $k(H_2O) = 1\ s^{-1}$. These values are considerably lower than those for $(CH_3O)_3C^+$ and $(C_2H_5O)_3C^+$.

(4) 2-Methoxy- and 2-Isopropoxy-1,3-dioxolane and 2-Methoxy-1,3-dioxane. These compounds were studied with the same methods as described in sections 1–3. The results are presented in Table II. It is noteworthy that IX^+, the cation from the dioxolane, is the most reactive species of the trialkoxy carbocations investigated, with respect to both H_2O and OH^-. The stability in H_2O increases considerably by introducing an additional methylene group into the system: the dioxane cation XI^+ lives five times longer in water than does IX^+. Replacement of methoxy by isopropoxy in the dioxolane system (see X^+, Table II) increases the lifetime of the cation by a similar factor.

(5) Conclusions on a Structure–Reactivity Relation for Trialkoxy Carbocations. With $(RO)_3C^+$ there is a very pronounced decrease in reactivity with respect to H_2O and OH^- in the series R = methyl, ethyl, isopropyl. This trend is expected on the basis of both electronic and steric effects, but with the limited number of substituents in this study these are not easily separated. In Figure 3 plots for the reactions of $(RO)_3C^+$ with H_2O and OH^- are shown by using σ^* constants. The three points for methyl, ethyl, and isopropyl lie reasonably well on straight lines whose slopes correspond to ρ^* values of +5.7 (for H_2O) and +3.7 (for OH^-).[23] Plots vs. the E_s substituent constants (not shown) are not nearly so linear, principally because methyl and ethyl have very similar values of E_s. These observations suggest that electronic factors are the more important, i.e., that the lifetime increase in going from R = methyl to R = isopropyl is caused more by thermodynamic stabilization of the cations than by enhanced persistence resulting from steric inaccessibility at C_α. This conclusion, however, must be viewed with caution pending more detailed studies of the substituent effect currently in progress.

In this connection, the difference between the two cyclic cations IX^+ and XI^+ is also interesting. In general, reactions converting a carbon atom from sp^2 to sp^3 hybridization are faster with six-atom rings as compared to five-atom ring systems,[24] whereas the reverse is observed here, the dioxolane cation being more reactive than the dioxane. This finding parallels that made in studies of cyclic ortho ester hydrolysis, where the conclusion was also reached that the dioxolane cation is less stable.[25] In that work an explanation was invoked in terms of ring strain and torsional strain, considering that there are in fact three atoms, the carbon and two ring oxygen atoms, which undergo changes in hybridization. The alternative explanation invokes the large electronic effect suggested above: In the case of the dioxane XI^+, the electron-donating mesomeric (+M) effect at C_α of one alkoxy substituent is not counteracted by the electron-withdrawing inductive (−I) effect of the other alkoxy substituent at C_β (as with IX^+). The overall electron donation to C_α is therefore greater in the case of the dioxane XI^+.

It is interesting to compare the $k(H_2O)$ values obtained in this study with those predicted by extrapolation of data from H_2SO_4–H_2O mixtures.[13] In the previous study[13] $(CH_3O)_3C^+$ was the only trialkoxy carbocation studied. Rate constants have now been obtained for the hydrolysis of the $(CH_3CH_2O)_3C^+$ cation in 68–77% H_2SO_4 (68.3%, 2.2×10^{-4} s^{-1}; 71.7%, 4.4×10^{-5} s^{-1}; 76.8%, 6.5×10^{-5} s^{-1}) and for the hydrolysis of the dioxolane IX^+ in 83–90% H_2SO_4 (83.4%, 8.1×10^{-4} s^{-1}; 85.7%, 1.9×10^{-4} s^{-1}; 88.0%, 5.0×10^{-5} s^{-1}; 90.2%, 1.4×10^{-5} s^{-1}). As described in detail previously[13] these can be extrapolated to purely aqueous solution by use of the formula $\log k(H_2O) = \log k(H_2SO_4) - \log (f_{R^+}a_{H_2O}/f_{\neq})$ where $k(H_2SO_4)$ is the rate constant measured in aqueous H_2SO_4 and $(f_{R^+}a_{H_2O}/f_{\neq})$ is the value for the general function describing cation reactivity in that acid. The assumption that is made here is that the ratio $f_{R^+}/f_{\neq}$ is independent of oxo carbocation structure. The $k(H_2O)$ estimates for these two cations and $(CH_3O)_3C^+$ are listed in Table II. Considering the extrapolation that is involved and the inherent assumption, these estimates show good agreement with the directly measured values.

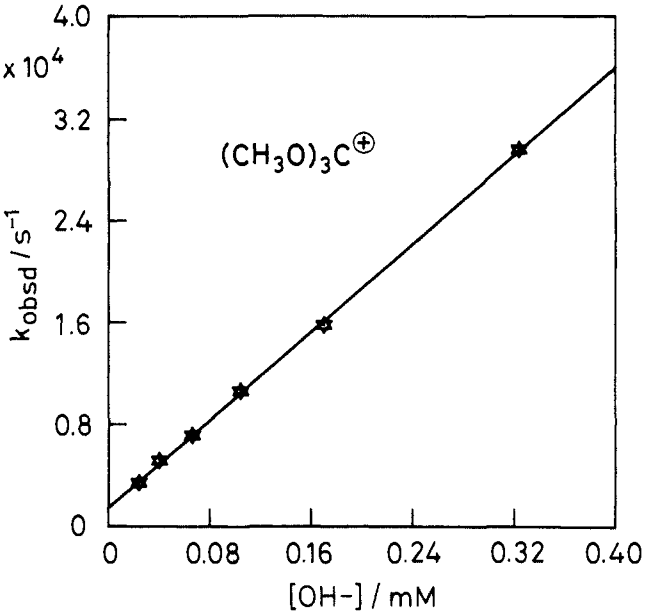
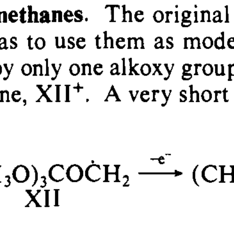


Figure 4. The dependence of k_{obsd} for the decrease of conductance on $[OH^-]$. $[(CH_3O)_4C]$ = 10 mM, $[IrCl_6^{2-}]$ = 0.13 mM.

Also noteworthy are the low values for $k(OH^-)$ found in this study. This result tends to support the suggestion[26] that the upper limit for rate constants for combination of oxyanions and carbocations may be below the diffusion range.

The activation parameters for reaction of $(CH_3O)_3C^+$ with water deserve special comment. Since the activation energy (7.6 kcal/mol) is not large, the low rate at room temperature results from the strongly negative activation entropy. This value can be explained as resulting from a combination of the loss of entropy associated with the bimolecular nature of the reaction and the solvation of the developing onium ion. On the basis of the similarity of the observed $\Delta S^{\neq}$ (−20 eu) to that (−24 eu)[27] for hydration of a proton by four water molecules a mechanism involving concerted proton transfer to solvent with a strong contribution of hydration of that proton is suggested, as shown below:



(6) Tetraalkoxymethanes. The original purpose of studying these compounds was to use them as model systems for carbocations substituted by only one alkoxy group, like, e.g., that from tetramethoxymethane, XII^+. A very short lifetime of such ions was anticipated.

$$\underset{}{(CH_3O)_4} \xrightarrow{-H^{\cdot}} \underset{XII}{(CH_3O)_3CO\dot{C}H_2} \xrightarrow{-e^-} \underset{XII^+}{(CH_3O)_3COC^+H_2} \quad (15)$$

However, on producing XII by H abstraction from tetramethyl orthocarbonate in the presence of $Fe(CN)_6^{3-}$ or $IrCl_6^{2-}$ at pH 9–11, a *slow* decrease of conductance was seen whose rate did not vary with the nature or concentration of oxidant (in the range 0.05–0.5 mM). The rate of the process was independent of ionic strength (varied by adding $NaClO_4$) but increased with pH according to $k_{obsd} = k(H_2O) + k(OH^-)[OH^-]$ (Figure 4). The $k(H_2O)$ and $k(OH^-)$ values obtained from this relation are $(1.5 \pm 0.2) \times 10^3$ s^{-1} and $(8.6 \pm 0.6) \times 10^7$ M^{-1} s^{-1} (Table II). These numbers are very similar to those for the reactions of the trimethoxymethyl

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[23] The ρ^* values were calculated taking account of the fact that there are three identical substituents at C_α. From these ρ^* values and the σ^* for *tert*-butyl a half-life of 40 s is calculated for the carbocation $((CH_3)_3CO)_3C^+$ in water at pH 7.

[24] Brown, H. C.; Ichikawa, K. *Tetrahedron* **1957**, *1*, 221.

[25] McClelland, R. A.; Gedge, S.; Bohonek, J. *J. Org. Chem.* **1981**, *46*, 886.

[26] Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1373.

[27] See: Buschmann, H.-J.; Dutkiewicz, E.; Knoche, W. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 129. Frost, A. A.; Pearson, R. G. "Kinetics and Mechansim"; Wiley: New York, 1953.

carbocation I^+ with H_2O and OH^- (eq 7 and 9), as obtained in the trimethoxymethane system. The rate constant measured at pH 6–6.5 is 1.4×10^3 s^{-1}, again the same as that obtained from the trimethoxymethane system. It is therefore concluded that it is I^+ which is produced also in the *tetra*methoxymethane system and that it is produced by C–O fragmentation (heterolysis)[28] from XII^+, as shown in eq 16.

$$\underset{XII^+}{(CH_3O)_3COC^+H_2} \rightarrow \underset{I^+}{(CH_3O)_3C^+} + CH_2O \qquad (16)$$

A major part of the driving force for reaction 16 probably results from the difference in stabilization energies between the mono- and the trialkoxy carbocations. At pH ≥9, there was no indication of a fast step that would result from hydrolysis of XII^+. The fragmentation (eq 16) must therefore be very fast. Since it is legitimate to assume (see section 1) that $k(XII^+ + H_2O) \geq 2 \times 10^7$ s^{-1}, $k(16)$ must be $\geq 2 \times 10^8$ s^{-1}. That the proposed fragmentation does not take place from the radical XII to give $(CH_3O)_3\dot{C}$ (I) followed by its oxidation was shown by in situ radiolysis–ESR studies (carried out on 10 mM tetramethoxymethane at pH ≈8): the radical XII ($a(H_\alpha)$ = 17.11 G, g = 2.003 12) was the only species detected, and there was no trace of I, which is easily seen on H abstraction from trimethoxymethane. These ESR experiments show that in the absence of oxidant the lifetime of XII is ≥ milliseconds. In the presence of ≥0.2 mM oxidant the lifetime of XII is reduced to microseconds (see Table I for the rate constants), giving it no chance at all to rearrange.

In order to test the hypothesis of carbocation fragmentation, experiments analogous to those described above were performed with tetra*ethoxy*methane. Reactions 17 and 18 describe the observations.

$$(C_2H_5O)_2C \xrightarrow{-H^\cdot} \underset{XIII}{(C_2H_5O)_3CO\dot{C}HCH_3} \xrightarrow{-e^-} \underset{XIII^+}{(C_2H_5O)_3COC^+HCH_3} \qquad (17)$$

$$XIII^+ \rightarrow \underset{III^+}{(C_2H_5O)_3C^+} + CH_3CHO \qquad (18)$$

As with the tetramethoxymethane system, the carbocation was identified as III^+ kinetically, i.e., by its $k(H_2O)$ value (Table II). ESR experiments showed that the rate of rearrangement of the radical XIII to yield acetaldehyde and III (followed by its oxidation) is too low at 20 °C to account for the formation of III^+ via this path. The conductance traces observed at pH ≥9 (see Figure 5) showed no evidence for a fast process of the kind expected for consumption of OH^- by the H^+ produced in the hydrolysis of the monoalkoxy carbocation $XIII^+$. The rate of fragmentation of $XIII^+$ according to eq 18 must therefore be a factor ≥10 larger than that for its hydrolysis (expected to be $\geq 2 \times 10^7$ s^{-1}, see section 1). The rate of fragmentation of $XIII^+$ is likely to be even larger than that of XII^+, due to (a) larger release of steric crowding and (b) the stabilizing influence[29] of the methyl group on the carbonyl bond of the aldehydic fragmentation product.

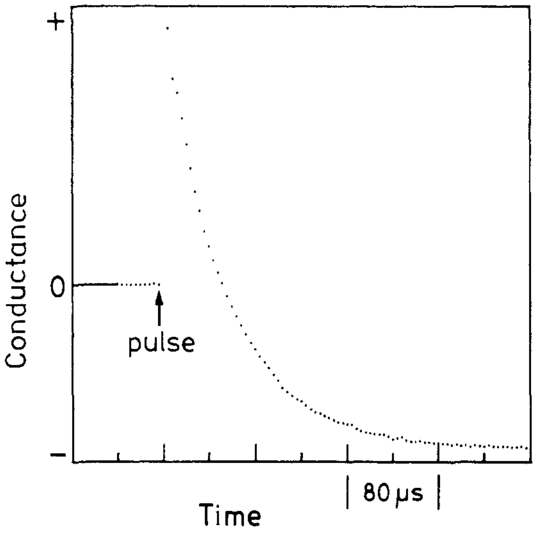

Figure 5. Conductance change observed after producing $(C_2H_5O)_3CO\dot{C}HCH_3$ in the presence of 0.1 mM $IrCl_6^{2-}$ at pH 10.5. $[(C_2H_5O)_4C]$ = 10 mM. The increase after the pulse is due to production of III^+ and $IrCl_6^{3-}$.

Summary and Conclusions. A method has been developed that uses pulse radiolysis to generate trialkoxy carbocations in aqueous solution. The rates of reaction of these carbocations with H_2O and OH^- were then directly measured with conductance techniques. It was found that these rates decrease very strongly with increasing electron-donating power (and steric hindrance) of the substituents (ρ^* = 5.7 and 3.7, respectively). Finally, evidence was presented for a C–O fragmentation reaction in which a monosubstituted alkoxyalkyl carbocation is converted into a much more stabilized trialkoxymethyl carbocation.

Registry No. I, 99702-89-3; I^+, 38091-69-9; II, 101418-94-4; III, 25748-60-1; III^+, 38092-02-3; IV, 25748-61-2; VI, 99704-03-7; VI^+, 101418-98-8; VII, 101418-95-5; IX, 19693-75-5; IX^+, 101418-99-9; X, 17230-31-8; X^+, 101419-00-5; XI, 73239-61-9; XI^+, 101419-01-6; XII, 101418-96-6; *i*-PrOPr-*i*, 108-20-3; $(MeO)_3CH$, 149-73-5; $(MeO)_4C$, 1850-14-2; $(EtO)_3CH$, 122-51-0; $(EtO)_4C$, 78-09-1; $(i\text{-}PrO)_3CH$, 4447-60-3; $Me_2CHOCMe_2^+$, 101418-97-7; $IrCl_6^{2-}Na_2^+$, 16941-25-6; $Fe(CN)_6^{3-}K_3^+$, 13746-66-2; $C(NO_2)_4$, 509-14-8; 2-isopropoxy-1,3-dioxolane, 75317-09-8.

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(28) There is literature precedence for such a reaction, albeit in a cyclic system: Kirby, A. J.; Martin, R. J. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1633.

(29) See: Steenken, S.; Schuchmann, H.-P.; von Sonntag, C. *J. Phys. Chem.* **1975**, *79*, 763 for an analogous effect on the fragmentation rates of α-alkoxyalkyl radicals.

(30) A fragmentation reaction may also occur with the monoalkoxy carbocations generated from the orthoformates, see eq 8. This reaction would produce an aldehyde and a dialkoxymethyl carbocation which would also be too short-lived[31] to be detected under the present experimental conditions.

(31) McClelland, R. A.; Steenken, S., unpublished material.