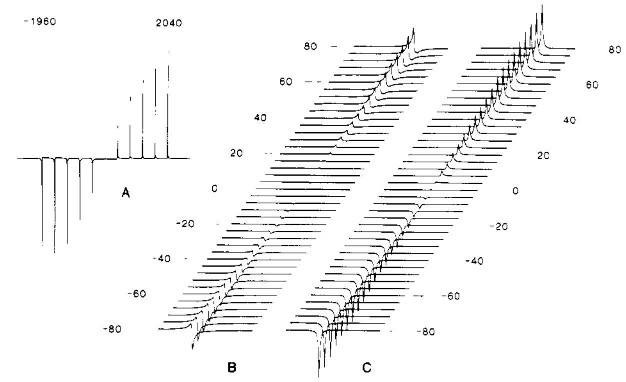

Figure 2. Demonstration of the spectral response in the JR and SJR sequences. The NMR lines from an H_2O sample are obtained for different offsets (indicated in Hz) between the proton Larmor frequency and the excitation frequency. (A) Coarse representation of the response to an SJR sequence ($\theta = 5.7°$, $\tau = 125$ μs). The small phase shifts described in the text are observed. Apart from these, a JR sequence would give the same results on this scale. The gain has been reduced by a factor 10 as compared to B and C. (B) The response to the same SJR sequence, in the range of small offsets. Notice the extensive cancellation, up to ±20 Hz; a dispersion component emerges first as offset is increased. (C) The small-offset response to a JR sequence ($\tau = 125$ μs). The amplitude is a linear function of offset and the mode is pure absorption for all offset values.

except quite close to the solvent frequency (Figure 2A)) may then be valuable.

Acknowledgment. We thank Dr. J. L. Leroy for his assistance in the experiments and Professor A. G. Redfield for helpful discussions.

Fast Hydrolysis of Alkyl Radicals with Leaving Groups in the β Position

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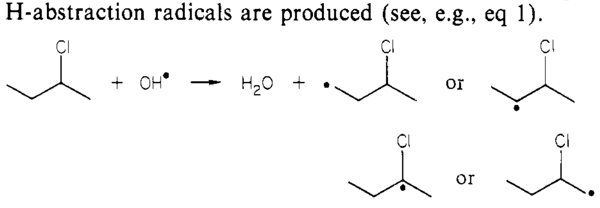
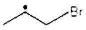
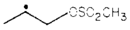
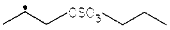
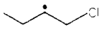
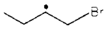
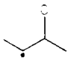
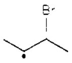
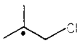
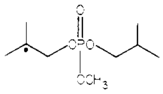
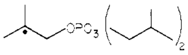
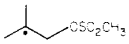
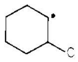
Upon reaction of radiolytically generated[1] OH radicals with alkyl bromides, alkyl chlorides, trialkyl phosphates, alkyl methanesulfonates, or dialkyl sulfates in aqueous solution, all possible H-abstraction radicals are produced (see, e.g., eq 1).



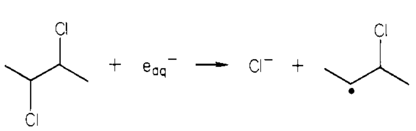
(1)

Some of these radicals give rise to rapid formation of acid (see Table I), as was found by time-resolved conductivity measurements upon pulse radiolysis.[2,3] The acid-forming radicals were identified in some instances as the β-substituted ones by specifically producing them, e.g., by reacting radiolytically generated[1] hydrated electrons, e_{aq}^-, with vicinal dihaloalkanes[4,5] (see e.g., eq 2).

Table I. First-Order Rate Constants of Acid Formation Observed by Time-Resolved[a] Conductivity Measurements upon Pulse Radiolysis[1,2] of N_2O-Saturated Aqueous Solutions of the Substrates Listed Below (10^{-3}–10^{-2} M) at pH 4.5–5 and 292 ± 3 K

substrate	radical undergoing hydrolysis[b]	rate constant of acid formation, s^{-1}
1-chloropropane		*c*
1- or 2-bromopropane[d]		7×10^3
1-propylmethanesulfonate		2×10^5
di-1-propyl sulfate		$\geqslant 10^6$
1-chlorobutane		*c*
1-bromobutane		
1-butylmethanesulfonate		$\geqslant 10^6$
2-chlorobutane		3.5×10^5
2-bromobutane	 or  [e]	$\geqslant 10^6$; 10^4
1-chloro-2-methylpropane		3.5×10^{4} [f]
methyl bis(2-methyl-1-propyl) phosphate		3×10^4
tris(2-methyl-1-propyl) phosphate		1.4×10^4
2-methyl-1-propyl-methanesulfonate		$\geqslant 10^6$
chlorocyclohexane		$\geqslant 10^6$

[a] The H-abstraction radicals are produced within the pulse duration of 1 μs. The rate constants were independent of dose rate (accuracy ±25%). Time resolution 10^{-6} s. [b] The radicals of this column are the most abundant ones among the β-substituted alkyl radicals; whether these radicals are in equilibrium with the isomeric radicals resulting from reverse 1,2-leaving-group shifts and the latter contribute to the hydrolysis remains an open question. [c] No acid formation; the first half-life of the second-order termination of radicals was mainly in the range 10^{-3}–10^{-2} s after the pulse, and the first-order decay constant of the radical is therefore $<10^2$ s^{-1}. [d] The H-abstraction radical XII (Chart I) undergoes a 1,2-Br shift to yield XIII prior to hydrolysis in a very fast reaction.[12] [e] Two processes were observed, one fast and unresolved, assigned from analogies to the hydrolysis of the first radical; the second radical is expected from the 1,2-Br shift[13] XIV → XV, and therefore its rate of hydrolysis is identical with the one observed after H abstraction from 1-bromobutane. [f] Accuracy ±5%.



(2)

The reaction of 2,3-dichlorobutane with e_{aq}^- leads to a fast ($k \geq 10^6$ s^{-1}) and a slower ($k = 3.5 \times 10^5$ s^{-1}) increase of conductivity. The fast one is assigned to reaction 2 and the slow one to the decay of the radical formed in that reaction. The slower kinetics was

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(1) Upon radiolysis of water, OH radicals and hydrated electrons, e_{aq}^-, are the main radical species formed. In the presence of N_2O the latter are transformed into OH radicals: $N_2O + e_{aq}^- \rightarrow OH\cdot + OH^- + N_2$. *tert*-Butyl alcohol was added instead of N_2O in order to observe the reaction of e_{aq}^- with substrate. See: Henglein, A., Schnabel, W., Wendenburg, J., Eds. "Einführung in die Strahlenchemie"; Verlag Chemie: Weinheim, 1969.

(2) For the technique and basic chemical considerations see: Klever, H. Ph.D. Thesis, Ruhr-Universität, Bochum, 1974. Applictions may be found in ref 9 and 14.

(3) We have also determined the acid formed upon ^{60}Co γ irradiations at low conversion of substrate by titration of H^+, Cl^-, or Br^- with use of ion-selective electrodes; the yields of acid/OH· were the same as derived from the size of the conductivity changes.

(4) The reaction VIII (Chart I) + $e^- \rightarrow Cl_2^-\cdot$ + butenes, as observed in frozen methanol by Mishra and Symons (Mishra, S. P.; Symons, M. R. C. *Tetrahedron Lett.* **1975**, *30*, 2597) was not observed in the aqueous phase.

(5) γ-Bromo- or γ-chloroalkyl radicals produced analogously did not lead to acid formation; α-bromo- or α-chloroalkyl radicals produced in this fashion did not lead to acid formation in most cases, although some of them gave rise to rather little formation of acid in the millisecond time range.

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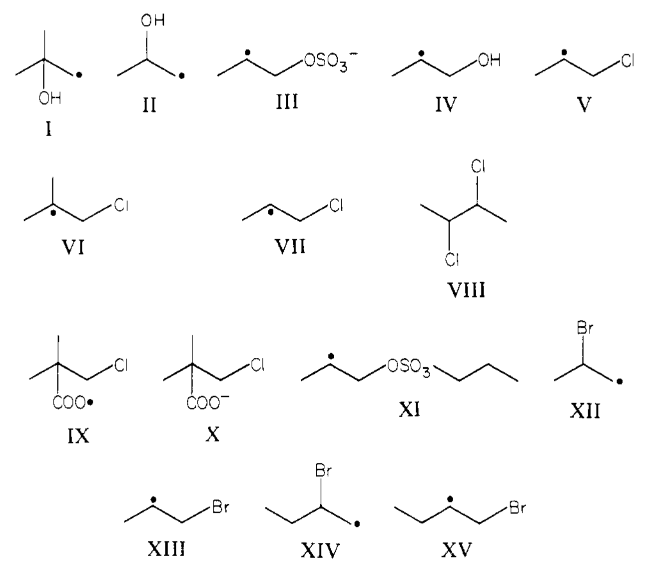
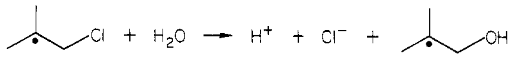
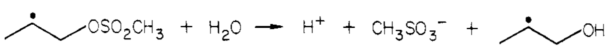
Chart I



the same as that observed after H abstraction from 2-chlorobutane (see eq 1 and the table). β-Hydroxyalkyl radicals—the products of hydrolysis—are formed upon decay of the radicals, as is shown by ESR spectroscopy[6,7] (see, e.g., eq 3 and 4).


(3)


(4)

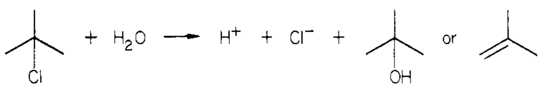
The radicals I and II (Chart I) were not observed. Allyl radicals resulting from elimination of HX (X = leaving group) were also not observed.

Olefins, the products of homolytic elimination of radicals X$\cdot$,[8] could not be detected by GLC among the reaction products. From pulse radiolysis combined with conductivity measurements olefins are expected[9] to react with $SO_4^{-}\cdot$ radicals[6,7] to yield β-SO_4^--substituted radicals rather than β-OH-substituted ones. We have confirmed this ESR spectroscopically, e.g., for propene at pH 9 where the radical[10] III but not IV was observed. If homolysis occurs,[11] it must be slower under our conditions than hydrolysis, cf. Table I.

From the table it is seen that there is a strong acceleration of rate of substitution of H by CH_3 in the α position to both the radical site or the leaving group, cf., e.g., V with VI or VII. Therefore, highly polar transition states are involved, suggesting an S_N1 type of hydrolysis of the radicals.

The new reactions may be regarded as analogous to the hydrolysis of α,α-dialkoxyalkyl[14] or α-alkoxyalkyl[15-17] radicals bearing leaving groups in the β position. In the former case α,α-dialkoxyalkene radical cations have been directly observed in aqueous solution as intermediates with half-lives on the order of milliseconds.[14] In the latter case α-alkoxyalkene radical cations are the intermediates with half-lives on the order of nanoseconds, as is inferred from scavenging reactions with HPO_4^{2-} ions.[18] Alkene radical cations are conceivable intermediates in the present systems. Scavenging with HPO_4^{2-} ions, however, was unsuccessful here; hence the half-lives of the alkene radical cations[19,20]—if they fully develop as such and are not only preformed in the transition states—are estimated to be shorter than 10^{-10} s in aqueous solution.

Compared with the known reaction of *tert*-butyl chloride with water[21] (see eq 5), which follows an S_N1 or E1 mechanism, respectively, reaction 3 is $\approx 5 \times 10^6$ times faster, corresponding to $\Delta\Delta G^{\ddagger}$ of $\approx$37 kJ/mol.


(5)

The enthalpies for the dissociation of Cl^- in the gas phase are 650 ± 4 kJ/mol for *tert*-butyl chloride and 640 ± 4 kJ/mol for the radical VI,[22] the difference being too small to account for the large difference in the rates of hydrolysis observed. The solvent isotope effect with reaction 3 was found to be $k_{H_2O}/k_{D_2O} = 1.6 \pm 0.1$, which is somewhat larger than the value of 1.35 observed for reaction 5. This indicates a larger degree of reorganization of the solvent shell in the transition state of the hydrolysis of the radical. The activation parameters of reaction 3 were determined to be $\Delta H^{\ddagger} = 38 \pm 4$ kJ/mol and $\Delta S^{\ddagger} = -30 \pm 20$ J/(mol K). From a comparison with the activation parameters of reaction 5,[23] $\Delta H^{\ddagger} = 91.8$ kJ/mol and $\Delta S^{\ddagger} = +35$ J/(mol K), it is suggested that there is a larger extent of solvation of the incipient ions in the transition state of reaction 3 compared with reaction 5.

Registry No. I, 5723-74-0; II, 7277-18-1; III, 83561-13-1; IV, 7055-10-9; V, 41895-36-7; VII, 42466-25-1; IX, 83561-12-0; X, 83561-11-9; XI, 83561-04-0; XII, 83561-09-5; XIII, 65149-63-5; XIV, 83561-10-8; XV, 55615-38-8; HO$\cdot$, 3352-57-6; $SO_4^-\cdot$, 12143-45-2; D_2O, 7789-20-0; 1-chloropropane, 540-54-5; 1-bromopropane, 106-94-5; 2-bromopropane, 75-26-3; 1-propyl methanesulfonate, 1912-31-8; di-1-propyl sulfate, 598-05-0; 1-chlorobutane, 109-69-3; 1-bromobutane, 109-65-9; 1-butyl methanesulfonate, 1912-32-9; 2-chlorobutane, 78-86-4; 2-bromobutane, 78-76-2; 1-chloro-2-methylpropane, 513-36-0; methyl bis(2-methyl-1-propyl) phosphate, 83561-02-8; tris(2-methyl-1-propyl) phosphate, 126-71-6; 2-methyl-1-propyl methanesulfonate, 16156-53-9; chlorocyclohexane, 542-18-7; 1-propyl methanesulfonate radical, 83561-03-9; 1-chlorobutane radical, 65161-22-0; 1-butyl methanesulfonate radical, 83561-05-1; 2-bromobutane radical, 83561-14-2; methyl bis(2-methyl-1-propyl) phosphate radical, 83572-92-3; tris(2-methyl-1-propyl) phosphate radical, 83561-06-2; 2-methyl-1-propyl methanesulfonate radical, 83561-07-3; chlorocyclohexane radical, 83561-08-4; *tert*-butyl chloride, 507-20-0.

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(6) The radical VI was selectively generated via IX as intermediate in H_2O in the ESR cavity by reacting photolytically produced $SO_4^-\cdot$ with X for analogies see: Madhavan, V.; Levanon, H.; Neta, P. *Radiat. Res.* **1978**, *76*, 15.

(7) The radical IV was the predominant species in the ESR spectrum after reaction of $SO_4^-\cdot$ with 1-propyl methanesulfonate in aqueous solution.

(8) Such reactions were frequently observed under other circumstances, particularly with β-bromoalkyl radicals; see, e.g.: Nonhebel, D. C., Walton, J. C., Eds. "Free Radical Chemistry"; University Press: Cambridge, 1974; pp 472–475.

(9) As was found, e.g., for cyclohexene, see: Chawla, O. P.; Fessenden, R. W. *J. Phys. Chem.* **1975**, *79*, 2693.

(10) By contrast the radical XI with the alkylated leaving group is not observed by ESR because if is too short lived (see Table), the radical IV being observed instead. By analogy large differences ($\Delta k \approx 10^3$ s^{-1}) in the rate constants of hydrolysis were observed with radicals $CH_3O\dot{C}HCH_2OPO_3^{2-}$ upon alkylation of the phosphate leaving group; see: Behrens, G.; Koltzenburg, G.; Ritter, A.; SchulteFrohlinde, D. *Int. J. Radiat. Biol.* **1978**, *33*, 163.

(11) Rather high rate constants have been reported for the formation of HX and Ph—CO—CH_2—CH_2—CH_2—CH=CH_2 from 1,4-diradicals Ph$\dot{C}$(OH)$CH_2CH_2\dot{C}HCH_2X$, e.g., 4×10^6 s^{-1} for X = Cl in benzene; the rate-determining step of these reactions is proposed to be homolytic β cleavage of X$\cdot$ assisted by solvent; see: Wagner, P. J.; Lindstrom, M. D.; Sedon, J. H.; Ward, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 3842.

(12) Skell, P. S.; Allen, R. G.; Gilmour, N. D. *J. Am. Chem. Soc.* **1969**, *91*, 6205.

(13) Skell, P. S.; Pavlis, R. R.; Lewis, D. C.; Shea, K. J. *J. Am. Chem. Soc.* **1973**, *95*, 6735.

(14) Behrens, G.; Bothe, E.; Koltzenburg, G.; Schulte-Frohlinde, D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 883; **1981**, 143.

(15) Gilbert, B. C.; Larkin, J. P.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 794.

(16) Behrens, G.; Koltzenburg, G.; Schulte-Frohlinde, D. In "Colloques Internat. du C.N.R.S. No. 278, Radicaux Libres organiques", Editions du C.N.R.S.: Paris, 1978; pp 117.

(17) Behrens, G.; Koltzenburg, G.; Ritter, A.; Schulte-Frohlinde D. *Int. J. Radiat. Biol.* **1978**, *33*, 163.

(18) Behrens, G.; Koltzenburg, G.; Schulte-Frohlinde, D., to be submitted for publication.

(19) In trifluoroacetic acid some alkene radical cations are sufficiently stable for ESR observation: Dessau, R. M. *J. Am. Chem. Soc.* **1970**, *92*, 6356.

(20) Alkene radical cations have recently been invoked as intermediates in aqueous solution in the acid-catalyzed 1,2-OH shifts of certain β-hydroxyalkyl radicals: Gilbert, B. C.; Normal, R. O. C.; Williams, P. S. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1401. Cf., however: Golding, B. T.; Radom, L. *J. Am. Chem. Soc.* **1976**, *98*, 6331. Here, radical-cation-like transition states are assumed for these reactions.

(21) k(hydrol) for *tert*-butyl chloride at 287 K is 6.4×10^{-3} s^{-1}: Laughton, P. M.; Robertson, R. E. *Can. J. Chem.* **1956**, *34*, 1714.

(22) Calculated from thermodynamic cycles and with data from Benson et al. (Benson, S. W.; Cruikshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279) and from Lossing and Semeluk (Lossing, F. P.; Semeluk, G. P. *Can. J. Chem.* **1970**, *48*, 955).

(23) Robertson, R. E.; Heppolette, R. L.; Scott, J. M. W. *Can. J. Chem.* **1959**, *37*, 803.