Reductive Halogen Elimination from Phenols by Organic Radicals in Aqueous Solutions; Chain Reaction Induced by Proton-Coupled Electron Transfer

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γ-Radiolysis and measurements of halide ions by means of ion chromatography have been employed to investigate reductive dehalogenation of chloro-, bromo-, and iodophenols by carbon-centered radicals, $^{\bullet}CH(CH_3)OH$, $^{\bullet}CH_2OH$, and $^{\bullet}CO_2^-$, in oxygen-free aqueous solutions in the presence of ethanol, methanol, or sodium formate. While the reactions of 4-IC_6H_4OH with $^{\bullet}CH(CH_3)OH$ and $^{\bullet}CH_2OH$ radicals are endothermic in water/alcohol solutions, the addition of bicarbonate leads to iodide production in high yields, indicative of a chain reaction. The maximum effect has been observed with about 10 mM sodium bicarbonate present. The complex formed from an α-hydroxyalkyl radical and a bicarbonate anion is considered to cause the enhancement of the reduction power of the former to the extent at which the reduction of the iodophenol molecule becomes exothermic. No such effect has been observed with phosphate, which is a buffer with higher proton affinity, when added in the concentration of up to 20 mM at pH 7. This indicates that one-electron reduction reactions by α-hydroxyalkyl radicals occur by the concerted proton-coupled electron transfer, PCET, and not by a two-step ET/PT or PT/ET mechanisms. The reason for the negative results with phosphate buffer could be thus ascribed to a less stable complex or to the formation of a complex with a less suitable structure for an adequate support to reduce iodophenol. The reduction power of the carbonate radical anion is shown to be high enough to reduce iodophenols by a one-electron-transfer mechanism. In the presence of formate ions as H-atom donors, the dehalogenation also occurs by a chain reaction. In all systems, the chain lengths depend on the rate of reducing radical reproduction in the propagation step, that is, on the rate of H-atom abstraction from methanol, ethanol, or formate by 4-$^{\bullet}C_6H_4OH$ radicals liberated after iodophenol dehalogenation. The rate constants of those reactions were determined from the iodide yield measurements at a constant irradiation dose rate. They were estimated to be 6 $M^{-1}\ s^{-1}$ for methanol, 140 $M^{-1}\ s^{-1}$ for ethanol, and 2100 $M^{-1}\ s^{-1}$ for formate. Neither of the tested reducing C-centered radicals was able to dehalogenate the bromo or chloro derivative of phenol.

1. Introduction

The processes leading to the degradation of halogenated aromatics are of particular interest for environmental remediation science and technology. These generally persistent and toxic classes of compounds are ubiquitously present in the environment and preferably of anthropogenic origin. In order to transform pollutants chemically, several methods involving the formation of free radicals known as advanced oxidation processes are in use and recognized as effective.[1,2] Strongly oxidizing hydroxyl radicals, $^{\bullet}OH$, are the most active initiators of usually complex reaction sequences leading finally to the degraded, less toxic, or nontoxic final products. Therefore, rate constants and mechanisms of reactions involving hydroxyl radicals have been most extensively studied and published in numerous publications.[3] Due to their high reactivity, hydroxyl radicals are highly unselective and able to react with almost any compound present in the system and not only with the target pollutant. This leads to lower efficiency of the method applied and, consequently, to higher costs.

Dehalogenation can be achieved also by reduction, hydrated electrons being efficient in this respect with almost any halogenated compound. Other radicals with reducing properties (such as α-amino or α-hydroxy carbon-centered radicals) can easily undergo one-electron reduction of a number of halogenated aliphatic compounds.[4,5] However, the elimination of a halide from aromatic compounds has been reported as operative only for the strongly reducing 2-propanol-derived radical anion in alkaline solutions,[6−9] $(CH_3)_2C^{\bullet}{-}O^-$, ($E° = -2.1$ V).[10] The reductive dehalogenation under anaerobic conditions with organic radicals in the presence of organic compounds might offer some advantages: (i) conditions for a chain reaction to occur can be achieved; (ii) most of the starting halogenated molecules, RX, are turned into the less complex and generally less toxic RH forms. The principle is shown in the Scheme 1, which represents the radiolysis as a method for primary radical production with alcohol as an organic additive. The hydroxy functional group is known to lower the α-C−H bond energy as well as to enhance the reduction power of C-centered radicals if directly attached to the radical center. Simple alcohols such as methanol, ethanol, and particularly, 2-propanol can, therefore, serve as decent hydrogen atom donors; α-hydroxyalkyl radicals derived from alcohols are, on the other hand, known as relatively good reducing agents.

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Scheme 1

$$\text{Solution} \rightsquigarrow \text{radicals } ({}^{\bullet}OH,\ e_{aq}^{-},\ {}^{\bullet}ROH,\ ...)$$

$$ {}^{\bullet}OH + R(OH)H \rightarrow {}^{\bullet}ROH + H_2O$$

$$e_{aq}^{-} + R'X \rightarrow R'^{\bullet} + X^{-}$$

$$ {}^{\bullet}ROH + R'X \rightarrow R'^{\bullet} + X^{-} + RO + H^{+}$$

$$R'^{\bullet} + R(OH)H \rightarrow R'H + {}^{\bullet}ROH$$

The aim of this work has been to find out conditions under which the selected organic free radicals with reductive properties would be able to transfer an electron to the halogenated phenols in aqueous solutions in the presence of organic additives and thereby initiate their dehalogenation, possibly in a chain process. The reducing radicals tested were ${}^{\bullet}CO_2^{-}$ and α-hydroxy carbon-centered radicals ${}^{\bullet}CH_2OH$ and ${}^{\bullet}CH(CH_3)OH$. They were formed by γ-irradiation of samples containing organic additives, sodium formate, methanol, or ethanol, in concentrations high enough for complete scavenging of primary water radicals ${}^{\bullet}OH$ and $H^{\bullet}$, reactions 2−4; the respective rate constants can be found in ref 3.[11] These compounds are inert toward hydrated electrons. The latter would be captured by halogenated phenols, reaction 5, the one-electron reduced intermediate of which would subsequently suffer the iodide release. Generally, the affinity to accept an electron increases in the chloro < bromo < iodo order of substituted organic compound, and for 4-chlorophenol, 4-bromophenol, and 4-iodophenol, it is already reflected in the rate constants reported for the strongest reductant, the hydrated electron, that is, $k_5 = 1.5 \times 10^9$, 6.3×10^9, and 1.0×10^{10} $M^{-1}\ s^{-1}$ for the three derivatives, respectively.[3,12] Primary water radicals and their yields (G values in units of μmol J^{-1}) produced by radiolysis of diluted aqueous solutions are shown in eq 1[13]

$$H_2O \rightsquigarrow e_{aq}^{-}\ (0.28),\ {}^{\bullet}OH\ (0.28),\ H^{\bullet}\ (0.06) \tag{1}$$

$$HCO_2^{-} + {}^{\bullet}OH/H^{\bullet} \rightarrow {}^{\bullet}CO_2^{-} + H_2O/H_2 \tag{2}$$

$$CH_3OH + {}^{\bullet}OH/H^{\bullet} \rightarrow {}^{\bullet}CH_2OH + H_2O/H_2 \tag{3}$$

$$CH_3CH_2OH + {}^{\bullet}OH/H^{\bullet} \rightarrow {}^{\bullet}CH(CH_3)OH + H_2O/H_2 \tag{4}$$

$$e_{aq}^{-} + XC_6H_4OH \rightarrow X^{-} + {}^{\bullet}C_6H_4OH\ (X = Cl, Br, \text{or } I) \tag{5}$$

$$2{}^{\bullet}C_6H_4OH \rightarrow HOC_6H_4{-}C_6H_4OH \tag{6}$$

$$ {}^{\bullet}C_6H_4OH + R^{\bullet} \rightarrow R{-}C_6H_4OH \tag{7}$$

$$ {}^{\bullet}C_6H_4OH + HCO_2^{-} \rightarrow C_6H_5OH + {}^{\bullet}CO_2^{-} \tag{8}$$

$$ {}^{\bullet}C_6H_4OH + CH_3OH \rightarrow C_6H_5OH + {}^{\bullet}CH_2OH \tag{9}$$

$$ {}^{\bullet}C_6H_4OH + CH_3CH_2OH \rightarrow C_6H_5OH + {}^{\bullet}CH(CH_3)OH \tag{10}$$

The fate of the phenyl radicals, ${}^{\bullet}C_6H_4OH$, formed in the reaction 5 would be radical−radical termination reactions 6 and/or 7 or abstraction of a hydrogen atom from organic additives to form phenol molecules and again reducing radicals, reactions 8−10. Under a constant irradiation dose rate, that is, a constant rate of radicals formation, the fraction of phenyl radicals reacting by H-abstraction would depend on the organic additive concentration and its ability to donate a H-atom, which increases in the order $CH_3OH < CH_3CH_2OH < HCO_2^{-}$. The absolute rate constants for reactions 8−10 are not known yet, but according to the values reported in the literature for some other carbon-centered radicals,[4,5] such reactions are slow to moderately fast. For example, for the ${}^{\bullet}C_6H_5$ radical, $k_9 = 1.2 \times 10^6$ $M^{-1}\ s^{-1}$ and $k_{10} = 4.4 \times 10^6$ $M^{-1}\ s^{-1}$; for the ${}^{\bullet}CH_3$ radical, $k_9 = 2.2 \times 10^2$ $M^{-1}\ s^{-1}$ and $k_{10} = 5.9 \times 10^2$ $M^{-1}\ s^{-1}$; for the ${}^{\bullet}CF_3$ radical, $k_9 = 8.0 \times 10^3$ $M^{-1}\ s^{-1}$, $k_{10} = 4.6 \times 10^4$ $M^{-1}\ s^{-1}$, and $k_8 = 3.4 \times 10^5$ $M^{-1}\ s^{-1}$. They are, however, high enough to allow chain dehalogenation to occur in case any of the reducing radicals would be able to transfer an electron to XC_6H_4OH, reactions 11−13

$$ {}^{\bullet}CO_2^{-} + XC_6H_4OH \rightarrow X^{-} + {}^{\bullet}C_6H_4OH + CO_2 \tag{11}$$

$$ {}^{\bullet}CH_2OH + XC_6H_4OH \rightarrow X^{-} + {}^{\bullet}C_6H_4OH + H^{+} + CH_2O \tag{12}$$

$$ {}^{\bullet}CH(CH_3)OH + XC_6H_4OH \rightarrow X^{-} + {}^{\bullet}C_6H_4OH + H^{+} + CH_3CHO \tag{13}$$

$$ {}^{\bullet}CO_2^{-} - e^{-} \rightarrow CO_2 \tag{14}$$

$$ {}^{\bullet}CH(CH_3)OH - e^{-} - H^{+} \rightarrow CH_3CHO \tag{15}$$

$$ {}^{\bullet}CH_2OH - e^{-} - H^{+} \rightarrow CH_2O \tag{16}$$

To our knowledge, except for $(CH_3)_2{}^{\bullet}CO^{-}$, no organic radicals have been reported to react with halogenated aromatics via electron transfer followed by halogen elimination from the reduced aromatic molecule, although some of them are relatively strong reducing agents. Thus, the standard reduction potential, $E°$, for the half reactions 14, 15, and 16 amounts to −1.9, −1.25, and −1.18 V, respectively.[10] However, while electron transfer from ${}^{\bullet}CO_2^{-}$ is somewhat hampered by relatively high internal reorganization energy,[14] the reaction with α-hydroxyalkyl radicals is accompanied by a release of a proton (reactions 12 and 13). It has been recently shown for a number of systems, where a proton-coupled electron-transfer mechanism operates, that the addition of a proton acceptor to the system can significantly enhance the electron-transfer rate constants or even allow an energetically unfavorable reaction to become favorable. This might happen in case they were coupled with proton transfer to the added base.[15−18] The possibility and efficiency of phenol dehalogenation by organic radicals in our systems was, therefore, tested in the presence of bicarbonate or phosphate buffers as additional proton acceptors. The occurrence of the dehalogenation reaction was monitored quantitatively by measuring the yield of Cl^{-}, Br^{-}, or I^{-} by means of ion chromatography.

2. Experimental Section

All chemicals were of analytical grade; ethanol, methanol, sodium bicarbonate, potassium dihydrogenphosphate and potas-

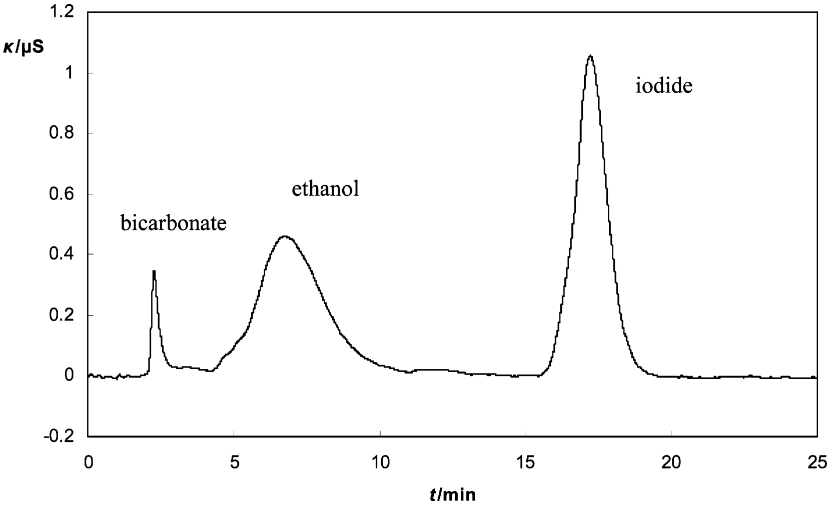

Figure 1. Characteristic ion chromatogram obtained for a γ-irradiated, oxygen-free neutral aqueous solution containing 1 mM 4-iodophenol, 0.3 M ethanol, and 10 mM sodium bicarbonate. The absorbed dose was 40.2 Gy; $[I^-] = 0.25$ mM.

sium hydrogenphosphate (Kemika), sodium formate (Fluka), and substituted phenols (Aldrich), were used as received from vendors. Solutions were prepared freshly before each experiment using water from a Millipore Milli-Q system. Shortly before irradiation, 5 mL of solutions was transferred into 10 mL irradiation glass vessels, sealed gas-tight by rubber septa, and bubbled with nitrogen (Messer Croatia plin, 99,999%) through solutions for about 15 min to remove oxygen.

Solutions were irradiated in the field of a ^{60}Co γ-source with a dose rate of about 155 Gy h^{-1} over the period of the investigations. The accurate dose rate was determined by Fricke dosimetry.[19]

After irradiation, halide concentrations were determined by means of ion chromatographic analysis with a Dionex DX-120 instrument consisting of an anion self-regenerating suppressor with a conductivity detector. An anion separation column, IonPac AS14 with an IonPac AG14 guard column, was used, and a solution containing 1 mM $NaHCO_3$ and 3.5 mM Na_2CO_3 as an eluent with a flow rate of 1.2 mL min^{-1} was also used. Appropriate standards were used for calibrations. A typical ion chromatogram obtained from the analysis of iodide formed upon radiolysis of 4-iodophenol in the presence of 0.3 M ethanol and 10 mM carbonate buffer is shown in Figure 1.

Radiation chemical yields are listed in terms of G values, the unit of which represents micromoles per joules of absorbed ionizing radiation energy. Error limits given for the specific numerical values refer only to the standard deviation of the mean of a series of single halogenide concentration versus absorbed dose measurements, usually 3−5 at different doses for each system. Absolute halogenide concentrations formed were kept in the region of up to about 30% conversion of XC_6H_4OH to avoid nonlinear correlation with the dose. Experiments were carried out at room temperature.

3. Results and Discussion

Iodophenols. The yield of iodide in an irradiated oxygen-free aqueous solution at about neutral pH and containing 1 mM 4-iodophenol was determined to be $G(I^-) = 0.33 \pm 0.02$ μmol J^{-1}. It did not change in the presence of 10 mM sodium bicarbonate added as a buffer (see Table 1). In the absence of any buffer, addition of ethanol to the solution in the concentration of 0.3 M decreased the iodide yield to $G(I^-) = 0.27 \pm 0.01$ μmol J^{-1}. While 4-iodophenol reacts very fast with all three primary water radiolysis radicals, $k(e_{aq}^-) = 1.0 \times 10^{10}$ M^{-1} s^{-1}, $k(^{\bullet}OH) = 9.3 \times 10^9$ M^{-1} s^{-1}, and $k(H^{\bullet}) = 7.8 \times 10^9$ M^{-1} s^{-1},[12] it seems that only reactions with hydrated electrons and H-atoms lead to iodide formation, and this is in about full yields, $G(e_{aq}^- + H^{\bullet}) = 0.34$ μmol J^{-1}. Obviously, the reaction with the hydroxyl radical does not contribute to the dehalogenation process for 4-iodophenol, although some contribution has been observed for 2-iodophenol.[12] Namely, upon addition of ethanol in the given concentration, all $^{\bullet}OH$ and $H^{\bullet}$ were scavenged by alcohol, and the drop of $G(I^-)$ by 0.06 μmol J^{-1} observed equals just the yield of $H^{\bullet}$ radicals. The result clearly indicates that 1-hydroxyethyl radicals are not able to transfer an electron to 4-iodophenol to produce iodide according to reaction 13.

TABLE 1: Yield of Iodide in γ-Irradiated Oxygen-Free Neutral Aqueous Solutions Containing 1 mM 4-Iodophenol in the Presence of Different Additives

organic additive	buffer	$G(I^-)$ μmol J^{-1}
–	–	0.33 ± 0.02
–	$NaHCO_3$ / 10 mM	0.33 ± 0.03
C_2H_5OH/ 300 mM	–	0.27 ± 0.01
C_2H_5OH/ 0.3 M	$NaHCO_3$ / 10 mM	5.7 ± 0.7
CH_3OH/ 0.3 M	$NaHCO_3$/ 10 mM	0.9 ± 0.1
C_2H_5OH/ 0.3 M	KH_2PO_4/K_2HPO_4 1:1/ 10 mM	0.41 ± 0.02
C_2H_5OH/ 0.3 M	KH_2PO_4/K_2HPO_4 1:1/ 20 mM	0.43 ± 0.01
$NaHCO_2$ / 0.01 M	–	2.5 ± 0.2

The situation did, however, dramatically change when the 4-iodophenol solution was irradiated in the presence of both ethanol and bicarbonate buffer. The high value of $G(I^-) = 5.7 \pm 0.7$ μmol J^{-1} (Table 1) unambiguously suggests the occurrence of dehalogenation in a chain process. In Table 1, more characteristic results are shown as obtained in some selected systems. Thus, methanol used instead of ethanol in the same concentration and in the presence of 10 mM bicarbonate is less effective. However, the yield of $G(I^-) = 0.9 \pm 0.1$ μmol J^{-1} achieved means not only an increase by a factor of about 3 if compared to the system with no alcohol or bicarbonate buffer added, but this is also a higher yield than the sum of all primary radicals from water radiolysis, which amounts to about 0.6 μmol J^{-1}. Interestingly, the addition of phosphate buffer at pH 7 ($H_2PO_4^-$/ HPO_4^{2-} = 1:1) has practically no effect upon iodide formation. At the total concentration of phosphate buffer of 10 and 20 mM, the iodide yield has increased only slightly at the same ethanol concentration of 0.3 M. Finally, the formate ion added to the system in the concentration of 10 mM and in the

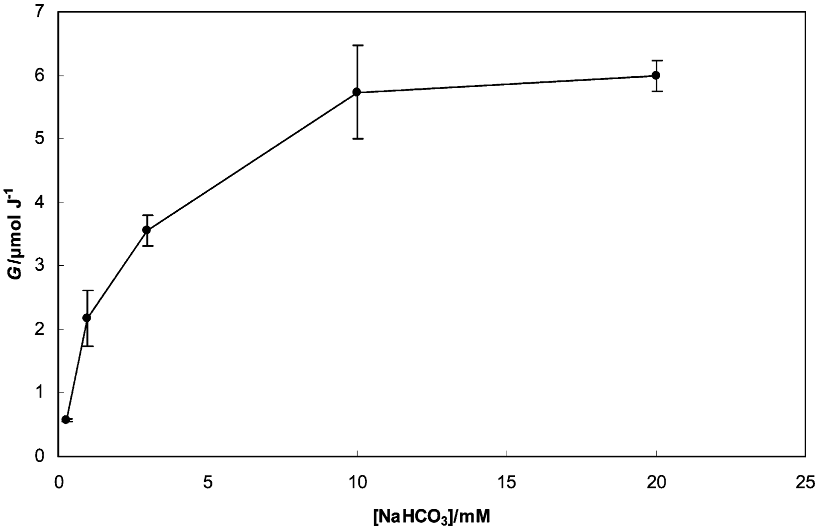

Figure 2. The yield of iodide, expressed as G/μmol J^{-1}, as a function of sodium bicarbonate concentration obtained in a γ-irradiated, oxygen-free aqueous solution at pH 7 containing 1 mM 4-iodophenol and 0.3 M ethanol.

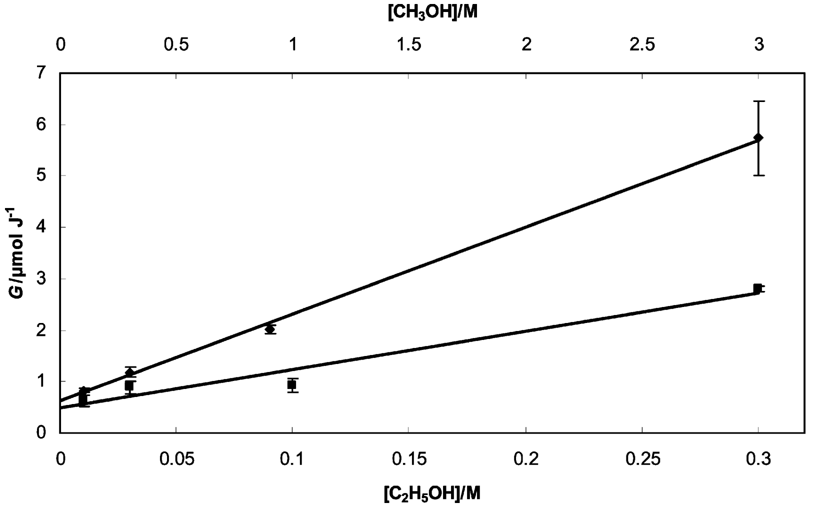

Figure 3. $G(I^-)$ versus the methanol (■) or ethanol (◆) concentration obtained in a γ-irradiated, oxygen-free neutral aqueous solution containing 1 mM 4-iodophenol and 10 mM sodium bicarbonate.

absence of any buffer has considerably increased the yield of iodide to a value characteristic for a chain process, that is, $G(I^-) = 2.5 \pm 0.2$ μmol J^{-1}. All of the systems above have been investigated in more detail, and the results are shown below.

In Figure 2, the yield of iodide is shown as a function of bicarbonate concentration as measured in γ-irradiated aqueous solutions containing 1 mM 4-iodophenol and 0.3 M ethanol. It can be seen that $G(I^-)$ increases first with an increase in bicarbonate concentration and then levels off at about 10 mM $NaHCO_3$. The dependence of $G(I^-)$ on alcohol concentration at a constant bicarbonate concentration of 10 mM is shown for methanol and ethanol as organic additives in Figure 3. Linear correlations are obtained for both alcohols, with ethanol being about 25 times more effective.

Keeping in mind that phosphate buffer at pH 7 has shown practically no influence on the dehalogenation process in the presence of ethanol (Table 1), the results can only be explained in terms of a specific complex formation between α-hydroxyalkyl radicals and the base, bicarbonate anions. It seems that the increase of the iodide yield in the presence of a bicarbonate buffer does not include deprotonation of an α-hydroxyalkyl radical to its anionic form that is a much better reducing species.[10] Such an anion might be able to subsequently transfer an electron to the iodophenol molecule, such as in reactions 17 and 18 written for the radical derived from ethanol. The other possibility, the enhanced proton accepting ability of the bulk in the presence of a buffer to take a proton from the protonated ketone formed after the electron transfer has occurred, thus promoting the overall reduction, reactions 19 and 20, does not seem feasible as well. Namely, because bicarbonate is a less strong base than the hydrogenphosphate anion, $pK_A(H_2CO_3/HCO_3^-) = 3.6$ and $pK_A(H_2PO_4^-/HPO_4^{2-}) = 7.2$, one would expect just the opposite from what has been obtained experimentally. In other words, the reduction by α-hydroxyalkyl radicals most probably does not proceed in two steps (proton transfer followed by electron transfer, reactions 17 and 18, or electron transfer followed by proton transfer, reactions 19 and 20). Akin to several other examples reported in recent years,[15−18] the mechanism seems to include formation of a complex, most probably a hydrogen-bonded association between the α-hydroxyalkyl radical and the base bicarbonate anion, reaction 21

$$^{\bullet}CH(CH_3)OH + B^- \rightleftharpoons BH + {^{\bullet}CH(CH_3)O^-} \qquad (17)$$

$$^{\bullet}CH(CH_3)O^- + 4\text{-}IC_6H_4OH \rightarrow {^{\bullet}C_6H_4OH} + I^- + CH_3CHO \qquad (18)$$

$$^{\bullet}\mathrm{CH(CH_3)OH} + 4\text{-}\mathrm{IC_6H_4OH} \rightarrow {}^{\bullet}\mathrm{C_6H_4OH} + \mathrm{I^-} + \mathrm{CH_3CHOH^+} \quad (19)$$

$$\mathrm{CH_3CHOH^+} + \mathrm{B^-} \rightleftharpoons \mathrm{BH} + \mathrm{CH_3CHO} \quad (20)$$

$$^{\bullet}\mathrm{CH(CH_3)OH} + \mathrm{B^-} \rightleftharpoons {}^{\bullet}\mathrm{CH(CH_3)OH\cdots B^-} \quad (21)$$

$$^{\bullet}\mathrm{CH(CH_3)OH\cdots B^-} + 4\text{-}\mathrm{IC_6H_4OH} \rightarrow \mathrm{I^-} + {}^{\bullet}\mathrm{C_6H_4OH} + \mathrm{BH} + \mathrm{CH_3CHO} \quad (22)$$

We believe that reactions 21 and 22 describe the process of iodide release correctly and that the species reacting with iodophenol is the α-hydroxyalkyl radical associated with the base bicarbonate. The reaction includes proton-coupled electron transfer, where an electron and proton are transferred to different acceptors 4-iodophenol and bicarbonate, respectively.

For the first time, the results demonstrate that aliphatic C-centered radicals with the hydroxy functional group attached directly to the radical center operate as reducing agents by the proton-coupled electron-transfer mechanism, similar to what has been reported for aromatic ketyl radicals.[15,20] The reduction power of these important and often-used reducing agents can be thus increased by the addition of a suitable base to the solution. It is worthwhile to note that bicarbonate, while effective as a base in the investigated systems, is, at the same time, a cheap, nontoxic, and environmentally friendly compound. Reduction potentials reported for α-hydroxyalkyl radicals in pure aqueous solutions, $E°(>\mathrm{C{=}O}, \mathrm{H^+}/>\mathrm{C^{\bullet}OH})$, should, therefore, refer to hydrogen-bonded water molecules acting as a base. Indeed, the reduction potential of α-hydroxyalkyl radicals shows a particularly large solvent effect. For $\mathrm{(CH_3)_2{}^{\bullet}COH}$, it amounts to −0.60 V versus SCE in acetonitrile.[21,22] However, it becomes more negative in more polar and protic solvents, −1.1 V in a 3:1 mixture of 2-propanol/acetonitrile[21] and −1.3 V in water.[23] It has been ascribed to the better ion solvation properties of the two latter solvents and their higher proton affinity assisting the follow-up proton loss from the protonated ketone formed after the electron transfer.[22] The proposed concerted proton-coupled electron-transfer mechanism seems to explain this effect in an even more obvious and straightforward way. The addition of water to acetonitrile solvent and the formation of a hydrogen-bonded diphenyl ketyl/water complex has been reported to decrease the endothermicity of the reduction of *N*-methoxypyridinium salts. This reaction also occurs by a proton-coupled electron-transfer mechanism.[20] A similar example, the formation of a hydrogen-bonded association of tyrosine with a hydrogen phosphate ion in aqueous solutions (maximum effect with a 50 mM phosphate buffer at pH 7.5), has been recently proposed to promote the electrocatalytic one-electron oxidation of tyrosine via a multisite electron−proton transfer.[18]

The results obtained in this work clearly show that in the presence of bicarbonate, the reduction power of α-hydroxyalkyl radicals is significantly enhanced, turning the endothermic reactions 12 and 13, where X is iodine, into energetically favorable ones, as shown for ethanol radicals by reaction 22. Experiments are underway in which it has been possible to achieve an enhancement of reductive chain dehalogenation upon buffer addition due to the acceleration of the electron-transfer rate for some halogenated compounds for which the reduction reactions with alcohol radicals, similar to reaction 13, are already exothermic.

The lack of an observable effect of the phosphate buffer in a concentration of up to 20 mM employed in this study might be due to the lower stability of the corresponding complex for the more bulky phosphate ions. The other possibility that might be put forward is a formation of a complex with a less suitable structure for the proton-coupled electron transfer to take place.

The high yields of iodide obtained in systems with methanol and ethanol, shown in Figures 2 and 3, indicate chain reactions, where reactions 3−5 are initiation reactions, reactions 21, 22, 9, and 10 lead to chain propagation, and radical−radical combination, such as reactions 6 and 7, terminate the chain. At the constant dose rate, that is, a constant rate of chain termination steps, k_t, the chain length seems to be limited by the establishment of equilibrium 21 at a lower bicarbonate concentration (up to 10 mM). At $[\mathrm{HCO_3^-}]$ above ∼10 mM, the rate of the hydrogen abstraction reaction from alcohol molecules by $^{\bullet}\mathrm{C_6H_4OH}$ becomes the limiting step, not the reduction reaction 22, which occurs most probably with a much higher rate. This is concluded from data shown in Figure 3 where the linear correlations have been obtained throughout the alcohol concentration range employed. From the half value of the typically equilibrium curve shown in Figure 2, which appears at about 2 mM bicarbonate, the equilibrium constant of $K_{21} \sim 500\ \mathrm{M^{-1}}$ has been estimated. According to the above arguments, the yield of $\mathrm{I^-}$ at bicarbonate concentrations ≥10 mM should be dependent only on the alcohol concentration, that is, on $k_{10}[\mathrm{C_2H_5OH}][{}^{\bullet}\mathrm{C_6H_4OH}]/2k_t[\text{radicals}]^2$ for ethanol and $k_9[\mathrm{CH_3OH}][{}^{\bullet}\mathrm{C_6H_4OH}]/2k_t[\text{radicals}]^2$ for methanol. Taking $2k_t \sim 1 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ as a reasonable value for the radical−radical termination rate constant, $G(\mathrm{R^{\bullet}}) = 0.6\ \mu\mathrm{mol\ J^{-1}}$ for the yield of primary water radicals and thus the yield of initiation reactions, the experimental dose rate of 155 Gy $\mathrm{h^{-1}}$, and applying the steady-state approximation (reaction 23),[24] $k_9 \approx 6\ \mathrm{M^{-1}\ s^{-1}}$ and $k_{10} \approx 140\ \mathrm{M^{-1}\ s^{-1}}$ has been calculated from the slopes of the straight lines in Figure 3

$$G(\mathrm{I^-}) = \frac{k_{9,10}}{\sqrt{2k_t}} \sqrt{\frac{G(\mathrm{R^{\bullet}})}{\text{dose rate}}}\,[\mathrm{ROH}] \qquad (23)$$

Irradiation of samples containing formate as the organic additive leads to the iodide formation released from 2-, 3-, and 4-iodobenzene in a chain reaction, as demonstrated in Figure 4, where $G(\mathrm{I^-})$ is plotted as a function of sodium formate concentration. For example, the yield of iodide measured for 4-iodophenol (1 mM) in the presence of 10 mM formate exceeds the yield in the absence of any additive by about 1 order of magnitude. Very similar yields have been obtained for 3-iodophenol, whereas for 2-iodophenol, even higher yields have been obtained. As expected, the addition of bicarbonate buffer (10 mM in the system with 1 mM 4-iodophenol and 10 mM formate) had no influence on the amount of iodide formed. The results can be explained by the ability of the $^{\bullet}\mathrm{CO_2^-}$ radical to transfer an electron to any of the three iodophenols that subsequently dehalogenate, that is, reaction 11 for X = I is an exothermic process. For this system, reactions 2 and 5 represent the chain initiation, 8 and 11 propagation, and termination occurs again by radical−radical combination processes. Similar to alcohol/bicarbonate-containing solutions, the chain length is determined by the rate of the H-atom abstraction, reaction 8, at the constant dose rate. From the slopes of the straight lines obtained for $G(\mathrm{I^-})$ as a function of formate concentration, Figure 4, $k_8 \approx 2100\ \mathrm{M^{-1}\ s^{-1}}$ has been obtained for both 3- and $4\text{-}{}^{\bullet}\mathrm{C_6H_4OH}$ and $\approx 4500\ \mathrm{M^{-1}\ s^{-1}}$ for $2\text{-}{}^{\bullet}\mathrm{C_6H_4OH}$ radicals produced upon dehalogenation from 3-, 4-, and 2-iodophenol, respectively. This was calculated by using eq 23 and the same parameters as those for the alcohol-containing systems above.

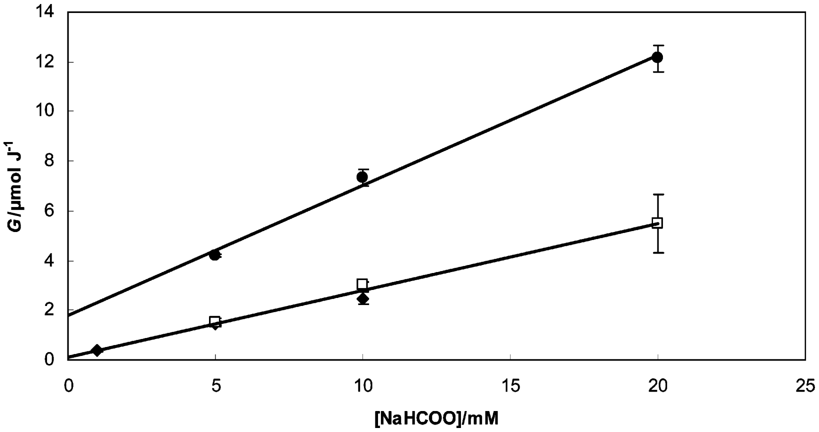

Figure 4. $G(I^-)$ versus the sodium formate concentration obtained in γ-irradiated, oxygen-free neutral aqueous solutions containing 1 mM 4-iodophenol (◆), 3-iodophenol (□), or 2-iodophenol (●).

Generally, the obtained rate constants for H-abstraction by $^{\bullet}C_6H_4OH$ radicals follow the known trend of $HCO_2^- > CH_3CH_2OH > CH_3OH$ for hydrogen-donating molecules.[4,5] The absolute values are, however, substantially lower than, for example, what has been reported for the reaction of a similar phenyl radical, $C_6H_5^{\bullet}$, with methanol and ethanol in aqueous solutions (see Introduction).

Bromo- and Chlorophenols. All attempts failed to produce Br^- from 4-bromophenol, 2-Br-4-Cl-phenol, or 4-Br-4-Cl-phenol in the reactions with organic radical $^{\bullet}CO_2^-$ (20 mM formate-containing systems) or with $^{\bullet}CH(CH_3)OH\cdots B^-$ (0.3 M ethanol/20 mM bicarbonate-containing systems). The measured yields have never exceeded $G(Br^-) \sim 0.3$ μmol J^{-1}, equal to the yield of bromide produced by the reaction with hydrated electrons according to reaction 5. The reduction power of the tested organic radicals is obviously not high enough to transfer an electron to, if compared with iodophenols, less electrophilic bromo derivatives. It is therefore concluded that reactions 11 and 22 with chlorophenol should be even more energetically unfavorable. Proving this experimentally by measuring the Cl^- yields has not been possible by the ion chromatography setup employed. Namely, the rather high concentration of salts (formate or bicarbonate anions) needed in the solutions to perform experiments has disturbed the quantitative chloride measurements due to very similar retention times of those ions.

4. Conclusion

It has been demonstrated that the reduction power of α-hydroxyalkyl radicals could be considerably enhanced in aqueous solution in the presence of bicarbonate buffer. Thus, $^{\bullet}CH(CH_3)OH$ and $^{\bullet}CH_2OH$ radicals derived from methanol and ethanol, while unreactive toward iodophenol in the absence of any buffer, cause liberation of iodide ions in a chain process in water/alcohol solutions upon addition of sodium bicarbonate, with a maximum effect at already only about 10 mM. This is explained by the formation of a complex between these radicals and the bicarbonate anion, most probably a hydrogen-bonded association, which changes the reduction potential of the α-hydroxyalkyl radical to the more negative value, thus allowing one-electron reduction of iodophenol to take place. The reaction is ascribed to the proton-coupled electron-transfer mechanism, where the electron is transferred to one molecule and the proton to another. The reduced iodophenol anion suffers the C−I bond rupture, releasing I^- and the $^{\bullet}C_6H_4OH$ radical. The latter species reacts further with alcohol molecules present in the system by H-atom abstraction to again produce α-hydroxyalkyl radicals, thus propagating the dehalogenation chain process.

In contrast to bicarbonate, the addition of phosphate buffer at pH 7 in the concentration of up to 20 mM had not led to the same effect. This is probably due to the less stable radical/buffer complex or to a complex of less suitable structure. Since phosphate buffer is a more potent proton acceptor, this result is taken as proof that the reduction by α-hydroxyalkyl radicals is not a two-step process; neither proton transfer followed by electron transfer nor electron transfer followed by deprotonation of the protonated ketone thus formed take place.

The carbonate radical anion, $^{\bullet}CO_2^-$, is shown to be a sufficiently strong reducing agent to reduce iodophenols by a one-electron-transfer mechanism. In the presence of formate ions as a source of radiolitically formed $^{\bullet}CO_2^-$, dehalogenation occurs also by a chain mechanism, with formate serving as the H-atom donor.

Quantitative measurements of the iodide yield at different alcohol or formate concentrations and constant bicarbonate concentration and irradiation dose rate enabled determination of the rate constants for H-atom abstraction by $^{\bullet}C_6H_4OH$ radicals. They ranged from 6 to about 4×10^3 M^{-1} s^{-1}, confirming the increasing H-atom donating ability in the order of methanol < ethanol < formate ion.

Neither of the tested reducing C-centered radicals was able to dehalogenate the bromo or chloro derivative of phenol.

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