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Thermochemical Properties of α-Hydroxy-Alkoxyl Radicals in Aqueous Solution

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Experimental kinetic data related to the reaction of carbonyl compounds with peroxynitrite anion, $ONOO^-$, in aqueous solutions was combined with estimated rate constants for the recombination of alkoxyl radicals with nitrogen dioxide. The equilibrium constants for O^- transfer from $ONOO^-$ and OH transfer from ONOOH to the carbonyls were derived and the Gibbs' energies of formation of the neutral and anionic α-hydroxy alkoxyl radicals were calculated. By means of these data the O−H bond strengths in carbonyl hydrates as well as reduction potentials of the alkoxyl radicals were obtained.

Introduction

There is a lack of knowledge concerning the thermochemistry of alkoxyl radicals in liquid solution, which stems from the instability of these radicals toward monomolecular rearrangements. One of these well-known processes is the so-called β-scission,[1] the reverse of the addition of carbon-centered radicals to C=O double bonds. The rate of β-scission was shown to increase with increasing polarity of the solvent,[2] and for the $(CH_3)_3CO^\bullet$ and $C_6H_5C(CH_3)_2O^\bullet$ radicals, the rate constants in water were determined to be as high as 1.4×10^6 [3] and 1.0×10^7 s^{-1},[4] respectively. Whenever the alkoxyl radical bears α-hydrogen atoms, a rapid 1,2-H shift occurs in protic solvents, such as water[5] and alcohols.[6] This rearrangement, which converts an alkoxyl radical into a α-hydroxy alkyl radical, has a rate constant well above 10^5 s^{-1}.[5−7] In contrast to the lack of knowledge concerning the thermochemistry of these radicals in water as well as in any other solvent, the O−H bond strengths in several aliphatic alcohols have been determined in the gas phase, and they were found rather insensitive to the alkyl group, ranging between 103 and 105 kcal/mol.[8] In a previous paper,[9] these gas-phase values were used to estimate the thermochemical properties of simple alkoxyl radicals in aqueous solutions. Though unstable, these radicals are important intermediates in several chemical, technical, environmental, and biological processes,[9] such as autoxidation or lipid peroxidation. The present work extends our estimations to α-hydroxy-alkoxyl radicals, which will be based on experimental data obtained in aqueous solution.

Discussion

In a recent work[10] the decomposition of peroxynitrite ion, $ONOO^-$, was studied in the presence of the prototypical carbonyl compounds, acetone and acetaldehyde. Scheme 1 was proposed to describe the reaction mechanism, where R is CH_3 or H.

Reactions 2 and 3 (characterized by k_2 and k_3) in the scheme are initiated by rate-determining homolyses along the weak O−O bond to form geminate pairs. The latter undergo rapid coupling reactions in the solvent cage to form molecular products (cage products), which in the present case are mainly nitrate and the initial carbonyl compound. A part of the geminate pairs diffuses out of the cage to form free alkoxyl and $^\bullet NO_2$ radicals. By studying the rate of disappearance of $ONOO^-$ in the presence of excess carbonyl compound as a function of pH and buffer concentration, we were able to determine experimentally a.o. K_1k_2, K_1k_{H2O}, and k_3/k_{OH}. Here, $K_1 = k_1/k_{-1}$, whereas the meaning of the other quantities clearly transpires from the scheme. In addition, we measured for both carbonyls the yield of free radicals[10] produced in reaction 2, denoted by α, and in reaction 3, denoted by β. All of these quantities are compiled in Table 1.

We can now introduce reactions 4 and 5, which are the decompositions of anionic and neutral carbonyl-OONO adducts into free alkoxyl and $^\bullet NO_2$ radicals:

$$RCH_3C(OONO)O^- \rightarrow RCH_3C(O^-)O^\bullet + {}^\bullet NO_2 \quad (4)$$

$$RCH_3C(OONO)OH \rightarrow RCH_3C(OH)O^\bullet + {}^\bullet NO_2 \quad (5)$$

As $k_4 = \alpha k_2$, we calculate $K_1k_4 = \alpha K_1k_2$ to be 1.8×10^{-3} and 20 M^{-1} s^{-1} for acetone and acetaldehyde, respectively. Similarly, $k_5 = \beta k_3$. Therefore, the low pH variant of K_1k_4, i.e., K_6k_5, can now be calculated as $K_6k_5 = \beta(K_1k_{H2O})(k_3/k_{OH})K_7/K_8$, where K_7 and K_8 are the acid dissociation constants of ONOOH and H_2O, respectively:

$$RCH_3C{=}O + ONOOH \rightleftharpoons RCH_3C(OONO)OH \; K_6 \quad (6)$$

$$ONOOH \rightleftharpoons ONOO^- + H^+ \quad K_7 = 2.5 \times 10^{-7}\ M\ (\text{ref } 11) \quad (7)$$

$$H_2O \rightleftharpoons OH^- + H^+ \qquad K_8 = 10^{-14}\ M^2 \quad (8)$$

With the values for K_7 and K_8 and the data in Table 1, we obtain $K_6k_5 = 1.4 \times 10^3$ M^{-1} s^{-1} for acetone and 3.6×10^6 M^{-1} s^{-1} for acetaldehyde.

The ultimate goal of this work is to obtain the values for the equilibrium constants K_9 and K_{10}:

$$RCH_3C{=}O + ONOO^- \rightleftharpoons RCH_3C(O^-)O^\bullet + {}^\bullet NO_2 \quad (9)$$

$$RCH_3C{=}O + ONOOH \rightleftharpoons RCH_3C(OH)O^\bullet + {}^\bullet NO_2 \quad (10)$$

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SCHEME 1

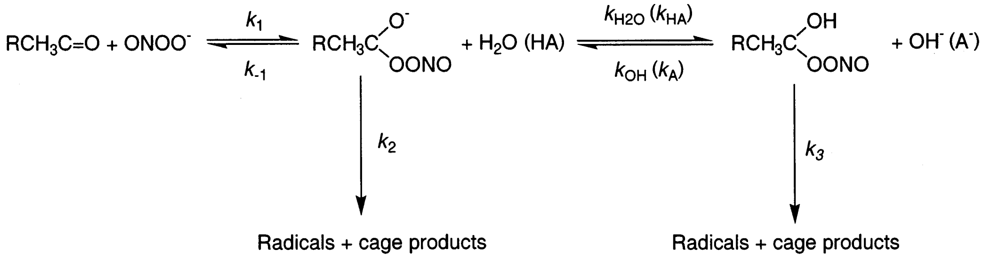

TABLE 1: Summary of the Experimental Data Referring to Scheme 1

	acetone	acetaldehyde
K_1k_2, $M^{-1}\ s^{-1}$	0.014 ± 0.003	115 ± 23
K_1k_{H2O}, $M^{-1}\ s^{-1}$	1.15 ± 0.02	1265 ± 35
k_3/k_{OH}, M	$(3.3 \pm 0.2) \times 10^{-4}$	$(7.1 \pm 0.8) \times 10^{-4}$
α	0.13	0.17
β	0.15	0.16

This requires good estimates for the rate constants k_{-4} and k_{-5}, because $K_9 = K_1K_4 = K_1k_4/k_{-4}$ and $K_{10} = K_6K_5 = K_6k_5/k_{-5}$. We consider the following reactions that take place at high pH:

$$\mathrm{RCH_3C(O^-)O^\bullet + {}^\bullet NO_2 \rightarrow products}\ k_{11} = k_{-4} + k_{-4a} \quad (11)$$

$$\mathrm{RCH_3C(O^-)O^\bullet + {}^\bullet NO_2 \rightarrow RCH_3C(OONO)O^-}(-4)$$

$$\mathrm{RCH_3C(O^-)O^\bullet + {}^\bullet NO_2 \rightarrow RCH_3C(O^-)ONO_2{}^-}(-4a)$$

Reaction −4a is then rapidly followed by reaction 12, which forms the stable end products:

$$\mathrm{RCH_3C(O^-)ONO_2{}^- \rightarrow RCH_3C{=}O + NO_3{}^-} \quad (12)$$

The corresponding reactions at low pH are

$$\mathrm{RCH_3C(OH)O^\bullet + {}^\bullet NO_2 \rightarrow products}\ k_{13} = k_{-5} + k_{-5a} \quad (13)$$

$$\mathrm{RCH_3C(OH)O^\bullet + {}^\bullet NO_2 \rightarrow RCH_3C(OONO)OH}(-5)$$

$$\mathrm{RCH_3C(OH)O^\bullet + {}^\bullet NO_2 \rightarrow RCH_3C(OH)ONO_2}(-5a)$$

Again, reaction −5a is followed by reaction 14:

$$\mathrm{RCH_3C(OH)ONO_2 \rightarrow RCH_3C{=}O + NO_3{}^- + H^+} \quad (14)$$

TABLE 2: Gibbs Energies, $\Delta_fG°$(kcal/mol), and pK_a values for the α-Hydroxy-Alkoxyl Radicals

	R = CH_3	R = H
$RCH_3C(OH)O^\bullet$	-38.3 ± 1.0	-36.4 ± 1.0
$RCH_3C(O^-)O^\bullet$	-21.3 ± 1.0	-20.2 ± 1.0
pK_a (radical)	12.5 ± 1.0	11.9 ± 1.0

The rate constants for radical recombination (reactions 11 and 13) cannot be determined experimentally, because alkoxyl radicals are very unstable with respect to 1,2-H shift and/or β-scission. However, it is known that alkyl peroxyl radicals react with $^\bullet NO_2$ at close to diffusion-controlled rates,[10] the rate constants having values of ca. $2 \times 10^9\ M^{-1}\ s^{-1}$. Given that alkoxyl radicals, just like peroxyl radicals, are oxygen-centered, it is reasonable to set their rate constants for reaction with $^\bullet NO_2$ to $2 \times 10^9\ M^{-1}\ s^{-1}$. Reaction 11 can take place via O−O coupling (reaction −4) or O−N coupling (reaction −4a). The latter reaction should then be followed by a very rapid, i.e., non-rate-determining, heterolysis (reaction 12), to yield nitrate and the carbonyl compound. In the acidic case, i.e., reaction 13, a similar scenario, described by reactions −5, −5a, and 14, applies. The reactions of $^\bullet NO_2$ with $^\bullet OH$ and $O^{-\bullet}$ were shown to result in approximately equal fractions of O−O and N−O coupling.[12] As we are dealing with oxygen-centered radicals in the present case as well, it is assumed that $k_{-4} \approx k_{11}/2$ and $k_{-5} \approx k_{13}/2$. This results in both rate constants k_{-4} and k_{-5} being ca. $10^9\ M^{-1}\ s^{-1}$ for acetone as well as for acetaldehyde. These values are believed to be accurate within better than 1 order of magnitude, i.e., $k_{-4} \approx k_{-5} = (0.3-3) \times 10^9\ M^{-1}\ s^{-1}$. With these assumptions, we obtain $K_9 \approx 1.8 \times 10^{-12}$ and $K_{10} \approx 1.4 \times 10^{-6}$ for acetone and $K_9 \approx 2 \times 10^{-8}$ and $K_{10} \approx 3.6 \times 10^{-3}$ for acetaldehyde. From these figures, we derive $\Delta G°_9 \approx 16.0$ kcal/mol and $\Delta G°_{10} \approx 8.0$ kcal/mol for acetone, and the corresponding values for acetaldehyde are ≈10.5 and ≈3.3 kcal/mol. In aqueous solution, the Gibbs energies of acetone and unhydrated acetaldehyde are known: with $\Delta_fG°((CH_3)_2CO) = -38.6$ kcal/mol[13] and $\Delta_fG°(CH_3CHO) = -32.0$ kcal/mol.[13] Furthermore, $\Delta_fG°({}^\bullet NO_2) = 15.1$ kcal/mol,[14] $\Delta_fG°(ONOO^-) = 16.4$ kcal/mol,[15] and $\Delta_fG°(ONOOH) = 7.4$ kcal/mol.[15] By means of these data, the Gibbs energies of formation for the α-hydroxy-alkoxyl radicals treated in this work are obtained and presented in Table 2. The estimated error margins given in the table are mainly made up by the uncertainties in the estimated values of k_{-4} and k_{-5}, whereas the uncertainties in the other quantities give a much smaller contribution.

From the difference in the tabulated $\Delta_fG°$ values for neutral and anionic alkoxyl radicals, the pK_a values for deprotonation of the OH group of the neutral alkoxyl radicals can be calculated to be around 12. This implies that an oxygen atom depresses the alcoholic pK_a by 4−5 units. The hydration equilibria of acetaldehyde and acetone, as well as the pK_a values of their hydrated forms are known,[16] with $K_{15} = 2 \times 10^{-3}$, $K_{16} = 1.4$, p$K_a((CH_3)_2C(OH)_2) = 14.5$, and p$K_a(CH_3CH(OH)_2 = 13.6$:

$$\mathrm{(CH_3)_2C{=}O + H_2O \rightleftharpoons (CH_3)_2C(OH)_2} \quad (15)$$

$$\mathrm{CH_3CHO + H_2O \rightleftharpoons CH_3CH(OH)_2} \quad (16)$$

From these values, we calculate $\Delta_fG°((CH_3)_2C(OH)_2) = -91.6$ kcal/mol, $\Delta_fG°((CH_3)_2C(OH)O^-) = -71.8$ kcal/mol, $\Delta_fG°(CH_3CH(OH)_2) = -88.8$ kcal/mol, and $\Delta_fG°(CH_3CH(OH)O^-) = -70.3$ kcal/mol.

Let us denote the neutral hydrates by XOH and the corresponding neutral alkoxyl radicals by $XO^\bullet$. To calculate the gaseous O−H bond strengths, BDE, of XOH, we set BDE $\approx \Delta_fG°(XO^\bullet) - \Delta_fG°(XOH) + \Delta G°(XO^\bullet)_{aq\rightarrow g} - \Delta G°(XOH)_{aq\rightarrow g} + 56.4$ kcal/mol.[17] The last term contains parameters for the hydrogen atom and hydrogen molecule in the gas phase, as well as a small entropy-related term of the order of −0.4 kcal/mol.[18] $\Delta G°(XO^\bullet)_{aq\rightarrow g} - \Delta G°(XOH)_{aq\rightarrow g}$ is the difference in the $\Delta G°$ of transfer from water to gas of $XO^\bullet$ and XOH, respectively. It has been shown[19] that this difference is rather independent of

TABLE 3: Reduction Potentials vs. NHE

reaction	$E°$ (V)
$(CH_3)_2C(OH)O^\bullet + e^- + H^+ \rightarrow (CH_3)_2C(OH)_2$	2.31 ± 0.04
$(CH_3)_2C(O^-)O^\bullet + e^- + H^+ \rightarrow (CH_3)_2C(OH)O^-$	2.19 ± 0.04
$(CH_3)_2C(OH)O^\bullet + e^- \rightarrow (CH_3)_2C(OH)O^-$	1.45 ± 0.04
$CH_3CH(OH)O^\bullet + e^- + H^+ \rightarrow CH_3CH(OH)_2$	2.27 ± 0.04
$CH_3CH(O^-)O^\bullet + e^- + H^+ \rightarrow CH_3CH(OH)O^-$	2.17 ± 0.04
$CH_3CH(OH)O^\bullet + e^- \rightarrow CH_3CH(OH)O^-$	1.47 ± 0.04
$CH_3COOH + e^- + H^+ \rightarrow CH_3CH(OH)O^\bullet$	−2.53 ± 0.04
$CH_3COO^- + e^- + H^+ \rightarrow CH_3CH(O^-)O^\bullet$	−2.95 ± 0.04

X and amounts to about −2 kcal/mol. Thus, BDE($(CH_3)_2C(OH)O-H$) = 107.7 ± 1.5 kcal/mol and BDE($CH_3CH(OH)O-H$) = 106.8 ± 1.5 kcal/mol are calculated. It is readily seen that, within the error margins, these values are identical and are very close to the O−H bonds measured in the gas phase of ordinary alcohols.[8] It would seem that replacement of H by an OH group raises the O−H bond strength by 2−3 kcal/mol, a reasonable increment. The strength of the α-C−H bond in $CH_3CH(OH)_2$ has been estimated to be ca. 92 kcal/mol,[20] implying a stabilization by 14−15 kcal/mol of the α-dihydroxy alkyl radical, $(CH_3)(OH)_2C^\bullet$, as compared to its isomer, the α-hydroxy-alkoxyl radical, $CH_3CH(OH)O^\bullet$. This difference provides a substantial driving force for the 1,2-H shift.

Finally, by utilizing the Gibbs energies of formation of the relevant species, thermodynamical standard reduction potentials for the neutral and anionic α-hydroxy-alkoxyl radicals as well as the reduction potentials of acetic acid and acetate can be calculated. Here, we have utilized the additional Gibbs energies $\Delta_f G°(CH_3COOH) = -94.8$ kcal/mol[13] and $\Delta_f G°(CH_3COO^-) = -88.3$ kcal/mol.[13] The standard reduction potentials for the various cases are compiled in Table 3. Again, the error margins mainly reflect the largest uncertainties, namely, those in the estimated values of k_{-4} and k_{-5}. The potentials in entries 1, 2, 4, and 5 provide a measure of the strength of the O−H bond or, what is equivalent, the hydrogen abstraction capabilities of the neutral and anionic α-hydroxyl alkoxyl radicals. These potentials compare to those of the simple neutral alkoxyl radicals ($E° = 2.18 \pm 0.04$ V).[9] The proton-independent potentials of entries 3 and 6 reveal that these radicals are significantly stronger one-electron oxidants than simple alkoxyl radicals ($E° = 1.23 \pm 0.07$ V).[9] This is due, no doubt, to the inductive effect of the OH group. The potentials in the last two entries show that both the neutral and the anionic α-hydroxyl alkoxyl radicals of acetaldehyde are extremely powerful hydrogen donors. This rationalizes the observation[21] that these radicals are capable of undergoing a hydrogen atom transfer to $^\bullet NO_2$ already in the geminate pair.

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