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Reduction Potentials and Kinetics of β-Fragmentation Reactions of 4-Substituted Benzoylthiyl Radicals

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By means of pulse radiolysis, the one-electron reduction potentials of 4-substituted benzoylthiolates $E°$(4-XPhC(O)S$^•$/4-XPhC(O)S$^-$), where X is CH_3, CH_3O, CF_3, and CN, were measured in aqueous solutions. The kinetics of β-fragmentation reactions of the 4-XPhC(O)S$^•$ radicals to form the corresponding 4-XPh$^•$ radicals and COS (i.e., 4-XPhC(O)S$^•$ → 4-XPh$^•$ + COS) were also determined. The pK_as of the corresponding acids (4-XPhC(O)SH) were measured by a spectrophotometric method. Thus, the values of $E°$(4-XPhC(O)S$^•$, H$^+$/4-XPhC(O)SH) and the S−H bond strength of the 4-XPhC(O)S−H were calculated. The substituent effects on the redox potential, the pK_a, and the kinetics of their β-fragmentation reactions were examined.

Introduction

In our previous work, we have studied the radical reactions upon one-electron oxidation of benzoyl thiolate (PhC(O)S$^-$) and acetyl thiolate ($CH_3C(O)S^-$) in aqueous solutions by means of pulse radiolysis.[1,2] The resulting benzoylthiyl (PhC(O)S$^•$) and acetylthiyl ($CH_3C(O)S^•$) radicals have absorption spectra in the easily accessible wavelength region 300−550 nm. The reduction potentials of the couples PhC(O)S$^•$/PhC(O)S$^-$ and $CH_3C(O)S^•$/$CH_3C(O)S^-$ were thus measured, using $N_3^•/N_3^-$ (1.33 V versus NHE[3]) as a reference couple. The PhC(O)S$^•$ and $CH_3C(O)S^•$ radicals were found to undergo a β-fragmentation reaction to form the corresponding Ph$^•$ and $CH_3^•$ radicals, respectively, and COS. The rate of β-fragmentation and the activation energies of the reactions were also measured. The reaction kinetics and the thermochemical properties of these radicals were discussed and compared with those of their oxygen counterparts.

Studies of substituent effects on the reactivity of molecules and radicals are of long standing.[4−7] In recent years, several studies of substituent effects on thermochemical properties of aromatic radicals and radical cations have been performed, resulting in general structure−activity relationships for these types of compounds. The majority of these relationships are based on the Hammett equation, using the Hammett substituent constant, σ, or the Brown substituent constant σ^+.

The ionization constants of benzoic acids have been used to define the Hammett substituent constant σ.[5,8] The substituent effects on the reactivities of substituted benzoyloxyl radicals (X-PhC(O)O$^•$) have also been studied.[9]

In this work, we continue our studies on the 4-substituted benzoylthiolates (4-XPhC(O)S$^-$) in aqueous solution. The substituents (X) are electron-donating CH_3O and CH_3 groups and electron-withdrawing CN and CF_3 groups. The reduction potentials of the 4-substituted benzoylthiyl radicals $E°$(4-XPhC(O)S$^•$/4-XPhC(O)S$^-$), the pK_as of the 4-substituted thiobenzoic acids (4-XPhC(O)SH), and the rates of β-fragmentation of the 4-XPhC(O)S$^•$ radicals were determined, and the substituent effects on these properties were examined.

Experimental Section

Materials. 4-Methoxyl (CH_3O-), 4-methyl (CH_3-), 4-cyano (CN-), and 4-trifluoromethyl (CF_3-) thiobenzoic acids were prepared from their corresponding benzoyl chlorides (from Lancaster Synthesis, England) by the modified synthetic method for thiobenzoic acid according to the literature.[10−12] The crude products were purified by recrystallization from hexane and/or ether. The purity of the products was found to be sufficiently high for experimental purposes, as checked by comparing the melting points and the NMR spectra with the literature values. Sodium azide (NaN_3), sodium thiocyanate (KSCN), and sodium hydroxide (NaOH), obtained from Sigma-Aldrich, were of the highest purity commercially available and used as received.

The pK_a values of 4-substituted thiobenzoic acids were determined by a spectroscopic method based on the different spectral properties of the anions (4-XPhC(O)S$^-$) and undissociated acids (4-XPHC(O)SH).[13] The aqueous solutions of the acids or anions were prepared with different stoichiometric concentrations and/or in various phosphate buffers of measured pH.

Pulse radiolysis was performed using doses of 10−26 Gy/pulse, corresponding to 6×10^{-6} to 1.6×10^{-5} M radicals. The 3 MeV linear accelerator used has a pulse length of 6 ns. The computerized optical detection system has been described elsewhere.[14] Dosimetry was performed with a N_2O-saturated 10^{-2} M KSCN solution, taking $G\epsilon = 4.42 \times 10^{-3}$ Gy^{-1} cm^{-1} at 500 nm.[15]

All experiments were performed in N_2O-saturated aqueous solutions, and the primary radiation chemical yield of OH$^•$ radicals, G_{OH}, was set to 5.6×10^{-7} mol J^{-1}.[16] In N_2O-saturated solutions containing high concentrations (0.01−0.2 M) of NaN_3, OH$^•$ radicals are quantitatively converted into $N_3^•$ radicals. Solutions were prepared using Millipore-deionized water. The solutions of thiolate ion, 4-XPhC(O)S$^-$, were obtained by constantly adding an equimolar amount of NaOH to the acid solutions.

All experiments were carried out at room temperature (22 ± 2 °C).

Results

One-electron oxidation of 4-XPhC(O)S$^-$, where X represents CH_3O, CH_3, CF_3, and CN, by $N_3^•$ and $Br_2^{•-}$ yields the

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TABLE 1. Experimental Values of the Reduction Potentials (in V) of 4-XPhCOS$^\bullet$ Radicals, Rate Constants (in s^{-1}) of Their β-Fragmentation Reactions, pK_as of the 4-XPhC(O)SHs, and BDEs (in kcal/mol) of the S−H Bonds, along with the Rate Constants of the β-Fragmentation Reactions of the Aroyloxyl Radicals

X	pK_a of 4-XPhC(O)SH	$E°(A^\bullet/A^-)$	$E°(A^\bullet, H^+/AH)$[a]	BDE(4-XPhC(O)S−H)	k_5 of 4-XPhC(O)S$^\bullet$	k_6 of 4-XPhC(O)O$^\bullet$ [a]
CH_3	2.6	1.19	1.34	87	6.2×10^3	1.8×10^6 (CH_3CN)
CH_3O	2.8	1.17	1.34	87	4.1×10^3	3.4×10^5 (CCl_4) $\leq 2 \times 10^4$ (CH_3CN)
H	2.45	1.21	1.36	87.4	8.5×10^3	2×10^6 (CCl_4) 1.5×10^6 (CH_3CN)
CF_3	1.37	1.28	1.36	87	1.7×10^4	
CN	1.43	1.23	1.31	86	1.7×10^4	
Cl						1.4×10^6 (CCl_4) 2×10^6 (CH_3CN)

[a] See ref 9.

corresponding 4-XPhC(O)S$^\bullet$ radical.

$$4\text{-XPhC(O)S}^- + N_3^\bullet \rightarrow 4\text{-XPhC(O)S}^\bullet + N_3^- \quad (1)$$

$$4\text{-XPhC(O)S}^- + Br_2^{\bullet-} \rightarrow 4\text{-XPhC(O)S}^\bullet + 2Br^- \quad (2)$$

The transient optical spectra of the four 4-XPhC(O)S$^\bullet$ radicals, observed 2 μs after pulse irradiation, closely resemble that of the PhC(O)S$^\bullet$ radical, having similar extinction coefficients of 7900 M^{-1} s^{-1} at the maximum 460 nm[2]. This maximum absorption was used in all subsequent kinetics measurements. The rate constants of reactions 1 and 2 were found to be unaffected by the substituent, as their values are the same as those of the PhC(O)S$^\bullet$ radical formation ($\sim 3 \times 10^9$ M^{-1} s^{-1} and 6×10^9 M^{-1} s^{-1} for $Br_2^{\bullet-}$ and $N_3^\bullet$, respectively).[2]

The lifetimes of all four 4-XPhC(O)S$^\bullet$ radicals studied were found to be within the time scale of pulse radiolysis experiments. Thus, by applying the method used for the PhC(O)S$^\bullet$ radical, the reduction potentials of the thiyl radicals $E°$(4-XPhC(O)S$^\bullet$/4-XPhC(O)S$^-$) were measured with $N_3^\bullet/N_3^-$ as a reference couple.

Since the dissociation constants (pK_as) of the 4-XPhC(O)SH were previously unknown, we measured these values by a spectroscopic method.

Combining the $E°$(4-XPhC(O)S$^\bullet$/4-XPhC(O)S$^-$) and the pK_a values measured, the standard reduction potentials of $E°$(4-XPhC(O)S$^\bullet$, H$^+$/4-XPhC(O)SH) were calculated according to the following equation.

$$E°(A^\bullet, H^+/AH) = E°(A^\bullet/A^-) + 0.059\ pK_a \quad (3)$$

Since the standard reduction potentials are related to the bond dissociation energies (BDEs) via eq 4,[17,18]

$$\text{BDE(S−H in kcal/mol)} = 23.1E°(A^\bullet, H^+/AH) + 56 \quad (4)$$

where the constant 56 kcal/mol is calculated from the known reduction potential of alkylthiyl radicals (1.37 V versus NHE)[19] and taking the strength of a typical alkyl S−H bond in the gas phase (87.4 kcal/mol).[20] The experimental values of reduction potentials of the 4-XPhC(O)S$^\bullet$ radicals, pK_as, and S−H bond energies of the 4-XPhC(O)SHs are listed in Table 1.

Similar to the PhC(O)S$^\bullet$ radical, the 4-XPhC(O)S$^\bullet$ radicals are found to undergo β-fragmentation to form the corresponding substituted phenyl radicals and COS (reaction 5).

$$4\text{-XPhC(O)S}^\bullet \rightarrow 4\text{-XPh}^\bullet + \text{COS} \quad (5)$$

The first-order rate constants of reaction 5 for the four 4-XPhC(O)S$^\bullet$ radicals are determined in a way similar to that of the PhC(O)S$^\bullet$ radical.[2] In the pulse radiolysis experiments, the 4-XPhC(O)S$^\bullet$ radicals decayed by mixed first-order and second-order kinetics within the dose range applied. The first-order decay originates from reaction 5, while the second-order decay is due to radical recombination reactions which always exist as competing reactions. In our experiments, the rate of the initial part of the decay was plotted against its maximum optical density, which should be proportional to the dose applied. By extrapolating the straight line to zero absorption, the first-order component k_5 is obtained as the intercept. The rate constants obtained are listed in Table 1, along with the available literature values of the rate constants of β-fragmentation of the oxygen counterparts, 4-XPhC(O)O$^\bullet$ radicals (reaction 6).

$$4\text{-XPhC(O)O}^\bullet \rightarrow 4\text{-XPh}^\bullet + CO_2 \quad (6)$$

Discussion

It is shown in Table 1 that the reduction potentials of 4-XPhC(O)S$^\bullet$ radicals are affected by the substituent X, although to a limited extent. It is important to point out that the reduction potentials for the different substituents only vary by 0.11 V, which is a rather small range. However, since all the experiments are performed in the same way and against the same reference couple $N_3^\bullet/N_3^-$, the differences in the reduction potentials are more meaningful than their absolute values. The pK_a values of the 4-XPhC(O)SHs are also shown to be affected by the substituent X. However, the combination of the reduction potentials and the pK_as, that is, the values of $E°$(4-XPhC(O)S$^\bullet$, H$^+$/4-XPhC(O)SH) and the BDEs of S−H bonds, are shown to be virtually unaffected by the substituent.

The reduction potentials of the 4-PhC(O)S$^\bullet$ radicals and the pK_as of the 4-PhC(O)SHs are plotted against the Hammett substituent constant σ_p values, as shown in Figure 1.

Figure 1 shows that the two linear correlations are good if the points for the 4-CNPhC(O)SHs are not included. The equations derived from these Hammett plots are

$$E°(4\text{-XPhC(O)S}^\bullet/4\text{-XPhC(O)S}^-) = 1.21 + 0.14\sigma_p \quad (7)$$

$$pK_a(4\text{-XPhC(O)SH}) = 2.38 - 1.55\sigma_p \quad (8)$$

If we compare the magnitude of the substituent effects (ρ) on the one-electron reduction potential of the 4-X-PhC(O)S$^\bullet$ radicals with that of the 4-X-PhS$^\bullet$ radicals, we see that PhC(O)S$^\bullet$ ($E° = 1.21$ V versus NHE, $\rho = 0.14$) is much less sensitive to substituents than PhS$^\bullet$ ($E° = 0.69$ V versus NHE, $\rho = 0.43$).[21] This is in contrast to the general trend found for substituent effects on the one-electron reduction potential of benzene radical cations, where a higher potential of the unsubstituted parent compound usually implies an increased sensitivity to substituents.[22,23] The rationale for this is probably that the sulfur radical

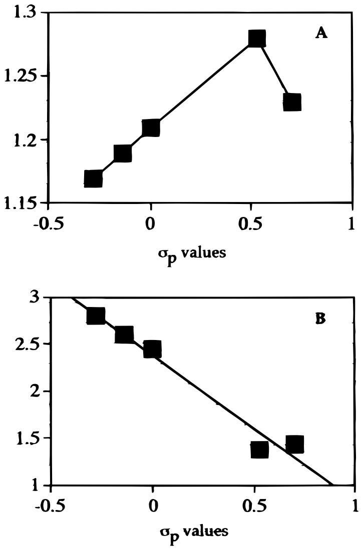

Figure 1. Reduction potential of the 4-PhCOS$^\bullet$ radicals (A) and pK_a of the 4-PhCOSH (B) plotted as a function of the Hammett substituent constant (σ_p) values.

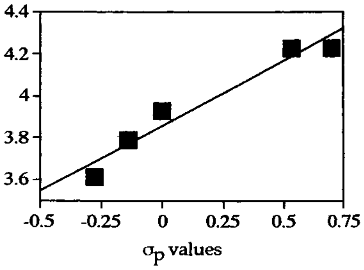

Figure 2. log(k_5) of β-fragmentation of 4-XPhCOS$^\bullet$ radicals plotted as a function of the Hammett substituent constant (σ_p) values.

in PhC(O)S$^\bullet$ is not directly connected to the ring, which lowers the sensitivity to ring substituents. An analogous case has been found when comparing substituent effects on reduction potentials of phenoxyl radicals and phenylperoxyl radicals. However, in this case, the effect of the extra oxygen in the phenylperoxyl radicals on the magnitude of the substituent effect is 1 order of magnitude (due to the strong resonance stabilization of the phenoxyl radical which is not present in the corresponding peroxyl radical).[24]

If we compare the magnitude of the substituent effects (ρ) on the pK_a values of 4-PhC(O)SH ($\rho = -1.55$) with that of 4-XPhC(O)OH, which is one by definition ($\rho = 1$), we see that PhC(O)SH is more sensitive to substituents.

The absence of substituent effects on the BDEs of 4-XPhC(O)SH is due to the isolating effect of the carbonyl group.

The rate constants for the β-fragmentation of the 4-X-PhC(O)S$^\bullet$ radicals, as shown in Table 1, are slightly affected by the electron-withdrawing and -donating character of the substituent. However, the rates of β-fragmentation of the oxygen counterparts, 4-XPhC(O)O$^\bullet$ radicals, are virtually unaffected by the substituent with the notable exception of 4-CH$_3$OPhC(O)O$^\bullet$, for which the β-fragmentation is significantly slower. For the 4-CH$_3$OPhC(O)O$^\bullet$ radical, there is also a significant solvent effect on the rate of β-fragmentation, judging from data in CCl$_4$ and CH$_3$CN. The rationale for both the substituent effect and the solvent effect is probably that, for strongly electron-donating substituents such as CH$_3$O, the radical becomes slightly zwitterionic and is thus more strongly solvated. This in turn makes the β-fragmentation thermodynamically less feasible. The zwitterion should be more stable in a polar solvent like CH$_3$CN than in CCl$_4$, which accounts for the observed solvent effect. For the 4-XPhC(O)S$^\bullet$ radicals, the substituent effect on the rate of β-fragmentation was expected to be small, since the difference in the rate of β-fragmentation between PhC(O)S$^\bullet$ and CH$_3$C(O)S$^\bullet$ is small.[1] In Figure 2 a plot of log k_5 against the Hammett constants for the 4-substituents is given.

Again, if the point for the 4-CNPhC(O)S$^\bullet$ radical is not included, the equation for this Hammett plot is

$$\log(k_5) = 3.87 + 0.723\sigma_p \tag{9}$$

Equation 9 shows that the substituent effect on β-fragmentation of 4-XPhC(O)S$^\bullet$ radicals is different from that of 4-XPhC(O)O$^\bullet$ radicals.

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