One-Electron Reduction Potential and the *β*-Fragmentation of Acetylthiyl Radical, Comparisons with Benzoylthiyl Radical and the Oxygen Counterparts

Rong Zhao,* Johan Lind, Gábor Merényi, and Trygve E. Eriksen

Department of Chemistry, Nuclear Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

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One-electron oxidation of acetyl thiolate ($CH_3C(O)S^-$) was achieved by hydroxyl ($OH\bullet$) and azide ($N_3\bullet$) radicals in aqueous solution. The resulting acetylthiyl radical ($CH_3C(O)S\bullet$) absorbs in the wavelength region 300−550 nm, with a maximum extinction coefficient of 3900 M^{-1} cm^{-1} at 440 nm. With $N_3\bullet/N_3^-$ as a reference couple, the reduction potential $E°(CH_3C(O)S\bullet/CH_3C(O)S^-)$ was measured to be 1.22 V vs NHE. Using a pK_a of 3.35 for thioacetic acid ($CH_3C(O)SH$), the standard reduction potential $E°(CH_3C(O)S\bullet, H^+/CH_3C(O)SH)$ is calculated to be 1.42 V vs NHE. This reduction potential implies that the S−H bond energy of $CH_3C(O)S-H$ is 88.6 kcal/mol (370.8 kJ/mol). The β-fragmentation of the $CH_3C(O)S\bullet$ radical, i.e., $CH_3C(O)S\bullet \rightarrow CH_3\bullet + COS$, was observed. Its kinetics was found to follow the Arrhenius equation, $\log(k_2/s^{-1}) = (12.3 \pm 0.1) - (10.1 \pm 0.2)/\theta$, where $\theta = 2.3RT$ kcal/mol. At 22 °C, the $CH_3C(O)S\bullet$ radical decays with a rate constant of 6.6×10^4 s^{-1}. The thermochemical properties of the $CH_3C(O)S\bullet$ radical and its β-fragmentation reaction are compared with those of the benzoylthiyl radical ($PhC(O)S\bullet$), as well as the corresponding oxygen counterparts, the acetyloxyl ($CH_3C(O)O\bullet$) and benzoyloxyl ($PhC(O)O\bullet$) radicals.

Introduction

Thiol acetic acid ($CH_3C(O)SH$) is commonly used in organic synthesis as a reagent for introduction of the thiol group into organic molecules.[1,2] The acetylthiyl moiety is also frequently seen in many important functional molecules (such as acetyl coenzyme A) in biological systems.[3] Despite its practical importance, the redox properties and the kinetic stability of the acetylthiyl radical ($CH_3C(O)S\bullet$) are not well studied. The interest for the radical chemistry of $CH_3C(O)S\bullet$ lies also in the fact that its oxygen analogue, the acetyloxyl radical ($CH_3C(O)O\bullet$) has an extremely high rate of β-fragmentation (reaction 1).

$$CH_3C(O)O\bullet \rightarrow CH_3\bullet + CO_2 \tag{1}$$

The rate constant k_1 was estimated to be ca. 10^9 s^{-1} [4,5] and experimentally determined to be less than 1.3×10^9 s^{-1}.[6] An understanding of the structure and kinetic character of the $CH_3C(O)S\bullet$ radical and a general comparison between the acyloxyl and acylthiyl radicals would be important to give an insight into the effects of replacing oxygen with sulfur.

The radical chemistry of acyloxyl ($RC(O)O\bullet$) has been a subject of interest for many years.[7−13] In comparison, the benzoyloxyl radical ($PhC(O)O\bullet$), formed by thermo- or photochemical decomposition of dibenzoyl peroxides has a longer lifetime; e.g., the β-fragmentation reaction 2 has a first-order rate constant of ca. 2×10^6 s^{-1} in CCl_4.[11]

$$PhC(O)O\bullet \rightarrow Ph\bullet + CO_2 \tag{2}$$

The spectroscopic characteristics and the kinetic properties of the $PhC(O)O\bullet$ radical are therefore well investigated.[11]

In our previous work, we have shown that one electron oxidation of benzoyl thiolate ($PhC(O)S^-$) in aqueous solutions produces the benzoylthiyl radical ($PhC(O)S\bullet$), which has a broad absorption spectrum in the wavelength region 350−500 nm.[14] The $E°(PhC(O)S\bullet/PhC(O)S^-)$ was measured to be 1.21 V vs NHE. The $PhC(O)S\bullet$ radical was found to undergo β-fragmentation (reaction 3) as evidenced by both kinetic analysis upon pulse radiolysis and product identification by GC-MS.

$$PhC(O)S\bullet \rightarrow Ph\bullet + COS \tag{3}$$

Reaction 3 has a rate constant of 8.5×10^3 s^{-1} at room temperature. In this paper, we report on $CH_3C(O)S\bullet$ radical formation upon one electron oxidation of acetyl thiolate ($CH_3C(O)S^-$) in aqueous solutions. The spectroscopic characteristics of the $CH_3C(O)S\bullet$ radical and the reduction potential of the $CH_3C(O)S\bullet/CH_3C(O)S^-$ couple resemble those of the $PhC(O)S\bullet$ radical. The kinetics of β-fragmentation of the $CH_3C(O)S\bullet$ radical (reaction 4) was also found to be similar to that of the $PhC(O)S\bullet$ radical, contary to the case with their oxygen counterparts, $CH_3C(O)O\bullet$ and $PhC(O)O\bullet$ radicals, where the difference in the rate of β-fragmentation is much larger.

$$CH_3C(O)S\bullet \rightarrow CH_3\bullet + COS \tag{4}$$

The thermochemical reasons behind this difference will also be discussed.

Experimental Section

Thioacetic acid ($CH_3C(O)SH$) (from Sigma), sodium azide (NaN_3), sodium thiocyanate (KSCN), and sodium hydroxide (NaOH) (from Sigma-Aldrich), were of the highest purity commercially available and used as received.

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.[15] 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.[16] The solution temperature was varied using a jacketed irradiation cell connected to a thermostatically con-

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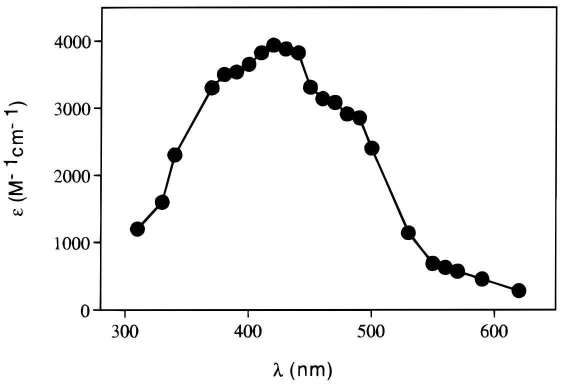


Figure 1. Transient absorption spectrum of acetylthiyl radicals observed 2 μs after electron pulse irradiation of an N_2O saturated solution containing 1×10^{-3} M $CH_3C(O)S^-$.

trolled water bath. A thermoelement probe was inserted into the outlet of the cell to measure the temperature of the irradiated solutions.

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}.[17] In N_2O-saturated solutions containing high concentrations (0.2−0.01 M) of NaN_3, OH• radicals are quantitatively converted into N_3• radicals. Solutions were prepared using Millipore deionized water. Since $CH_3C(O)SH$ is an acid ($pK_a = 3.36$)[18] with a strong odor, the solutions were prepared from NaOH solutions to form the thiolate ion, $CH_3C(O)S^-$. The pH was adjusted to ca. 8−9.

All experiments were carried out at room temperature (22 ± 2 °C), except for the Arrhenius plot measurements.

Results

Spectrum of the $CH_3C(O)S$• Radical. One-electron oxidation of $CH_3C(O)S^-$ by the OH• radical yields the $CH_3C(O)S$• radical, according to reaction 5.

$$CH_3C(O)S^- + OH\bullet \rightarrow CH_3C(O)S\bullet + OH^- \qquad (5)$$

The transient absorption observed 2 μs after electron pulse irradiation of an N_2O-saturated aqueous solution containing 1×10^{-3} M $CH_3C(O)S^-$ is shown in Figure 1.

The spectrum of $CH_3C(O)S$• exhibited a broad absorption peak in the region 300−550 nm, with a maximum located between 370 and 440 nm. The extinction coefficient at the maximum was measured to be 3900 M^{-1} cm^{-1} when the dithiocyanate radical anion $(SCN)_2^{-\bullet}$ was used as a reference.[17] The build-up rate of the $CH_3C(O)S$• absorption at 420 nm was titrated versus the CH_3COS^- concentration. The rate constant of reaction 5, obtained as the slope of a linear fit of the observed rates vs $[CH_3COS^-]$, was found to be 3×10^9 $M^{-1}s^{-1}$.

Reduction Potential of the $CH_3C(O)S^-/CH_3C(O)S$• Couple. The $CH_3C(O)S$• radical has a much longer lifetime (ca 10 μs, see below) than the $CH_3C(O)O$• radical (less than 1 ns[6]), which made possible the measurement of the reduction potential of the $CH_3C(O)S\bullet/CH_3C(O)S^-$ couple. The N_3• radical, having a reduction potential of 1.33 V,[19] rapidly oxidizes $CH_3C(O)S^-$ and was therefore chosen as the reference. When the N_3• radical oxidizes $CH_3C(O)S^-$, the following equilibrium is established.

$$CH_3C(O)S^- + N_3\bullet \rightleftharpoons CH_3C(O)S\bullet + N_3^- \qquad (6)/(-6)$$

In irradiated N_2O-saturated solutions containing varying concentrations of $CH_3C(O)S^-$ and N_3^-, with the latter in excess, the following relationship is obtained.

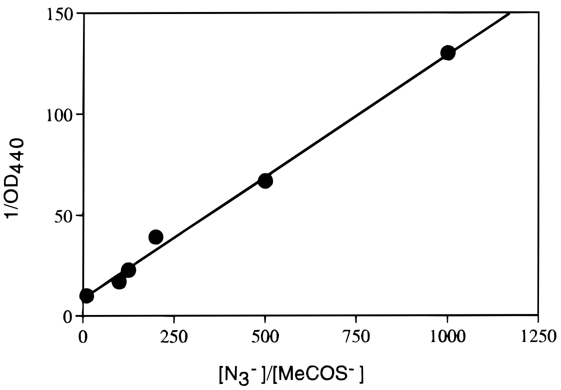


Figure 2. Inverse of optical density of $CH_3C(O)S$• radicals at 440 nm as a fuction of the ratio between N_3^- and $CH_3C(O)S^-$. The linear curve fit of the data is in accord with eq 7, and $K_6 = 80$ can be derived by dividing the intercept with the slope of the line.

$$OD°_{440}/OD_{440} = 1 + [N_3^-]/K_6[CH_3C(O)S^-] \qquad (7)$$

Here OD_{440} is the optical density at 440 nm of $CH_3C(O)S$• at equilibrium, K_6 is the equilibrium constant of reaction 6, and $OD°_{440}$ is the optical density when equilibrium 6 is completely shifted to the right. In the experiments, the concentrations of N_3^- and $CH_3C(O)S^-$ were chosen such that equilibrium 6 was reached before significant radical decay occurred. A plot of $1/OD_{440}$ versus $[N_3^-]/[CH_3C(O)S^-]$ is a straight line (Figure 2), and K_6 was found to be 80 by dividing the intercept by the slope of the line.

From the equilibrium constant K_6, we calculate $E°(CH_3C(O)S\bullet/CH_3C(O)S^-)$ to be 1.22 V vs NHE when a $E°(N_3\bullet/N_3^-)$ of 1.33 V is used as a reference. The pK_a of $CH_3C(O)SH$ is given as 3.36,[18] lower than that for its homologue, $CH_3C(O)OH$ (pK_a ca. 4.75).[20] Thus $E°(CH_3C(O)S\bullet, H^+/CH_3C(O)SH)$ is calculated to be 1.42 V vs NHE.

***β*-Fragmentation of the $CH_3C(O)S$• Radical.** The kinetics of $CH_3C(O)S$• radical β-fragmentation is studied by applying the same method used for the PhC(O)S• radical.[14] Kinetic traces were obtained by pulse irradiation of N_2O-saturated solutions containing 1×10^{-2} M $CH_3C(O)S^-$. The values of the initial part of the first-order decay rates were plotted against the maximal optical density, which should be proportional to the doses applied. By extrapolating the straight line to zero initial absorption (zero dose), the first-order component k_4 is obtained as the intercept. The rate constant k_4 was measured over a range of temperatures (10−60 °C, see Figure 3).

The Arrhenius plot for reaction 4 shown in Figure 3 yields the following temperature dependence:

$$\log(k_4/s^{-1}) = (12.3 \pm 0.1) - (10.1 \pm 0.2)/\theta \qquad (8)$$

where θ is 2.3*RT* kcal/mol and the error limits correspond to 2σ. Equation 8 gives an activation energy of 10.1 kcal/mol (42.3 kJ/mol) for reaction 4. At room temperature, k_4 is 6.6×10^4 s^{-1}.

Discussion

The spectrum of the $CH_3C(O)S$• radical resembles that of the PhC(O)S• radical but is somewhat blue shifted. The intensity at the maximum absorption (440 nm) is ca. half of that of the PhC(O)S• radical ($\epsilon_{460} = 7900$ M^{-1} cm^{-1}). The spectrum of the $CH_3C(O)S$• radical is mainly due to the resonance stabiliza-

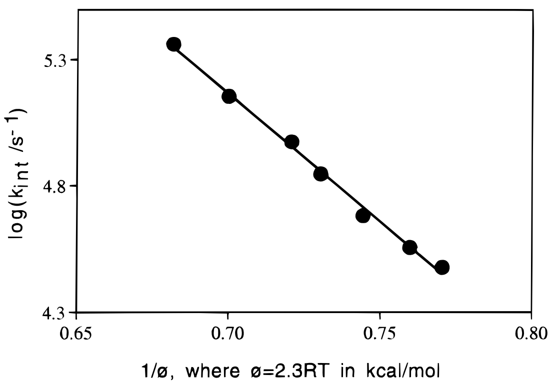


Figure 3. Arrhenius plot of log(k_4/s^{-1}) versus 1/θ, where $\theta = 2.3RT$ kcal/mol. The solutions are N_2O saturated and contain 1×10^{-2} M $CH_3C(O)S^-$.

TABLE 1: Summary of PK_a, Reduction Potential $E°$ in V, and BDE in kcal/mol for Thiol Acids and Their Oxygen Counterparts

	pK_a	$E°(A\bullet/A^-)$	$E°(A\bullet, H^+/A^-)$	BDE
$CH_3C(O)S-H$	3.35[a]	1.22[c]	1.42[c]	88.6[c]
$PhC(O)S-H$	2.48[a]	1.21[d]	1.36[d]	87.4[d]
$CH_3C(O)O-H$	4.75[b]	1.9[g]	2.2[g]	106.4[e]
$PhC(O)O-H$	4.19[b]	1.9[g]	2.1[g]	105.4[f]

[a] Reference 16. [b] Reference 18. [c] This work. [d] Reference 12. [e] Reference 21. [f] Calculated knowing the value of $\Delta H°_f(PhC(O)O\bullet) = -17$ kcal/mol, from ref 22. [g] Estimated from eq 9.

tion of the sulfur-centered radical by the carbonyl group. The enhanced absorption of the $PhC(O)S\bullet$ radical is an indication of some interactions between the $C(O)S\bullet$ moiety and the aromatic ring. For the oxygen analogues, the absorption from 500 to 700−800 nm of the $PhC(O)O\bullet$ radical was assigned to a transition localized on the $C(O)O\bullet$ moiety of the radical,[12] since the (alkoxycarbonyl)oxyl radical ($ROC(O)O\bullet$) was observed to have a similar absorption band in this region.[10] Consequently, one can assume that the acetyloxyl radical ($CH_3C(O)O\bullet$) absorbs similarly to the benzoyloxyl radical.

The reduction potential of the $CH_3C(O)S\bullet$ radical is found to be rather close to that of the $PhC(O)S\bullet$ radical. As a result of a slightly higher pK_a of $CH_3C(O)SH$, the standard reduction potential $E°(CH_3C(O)S\bullet, H^+/CH_3C(O)SH)$ is ca. 60 mV higher than $E°(PhC(O)S\bullet, H^+/PhC(O)SH)$. Since the standard reduction potential in solution is related to the bond dissociation energy via eq 9,[21,22]

$$\text{BDE(kcal/mol)} = 23.1E°(A\bullet/A) + 1.36\text{p}K_a + 56 \quad (9)$$

the bond enthalpies of $CH_3C(O)S-H$ and $PhC(O)S-H$ in the gas phase are calculated to be 88.6 and 87.4 kcal/mol, respectively. For the oxygen analogues, the experimental values of the enthalpy of formation, $\Delta H°_f(CH_3C(O)O\bullet)$ and $\Delta H°_f(PhC(O)O\bullet)$, are reported to be −49.5[23] and −17 kcal/mol,[24] respectively. These values were derived from the experimental value of $\Delta H°_f(RC(O)OO(O)CR)$ and the BDE of $RC(O)O-O(O)CR$.[25] As the $\Delta H°_f(CH_3C(O)OH)$ and $\Delta H°_f(PhC(O)OH)$ are −103 and −70.3 kcal/mol,[26] respectively, we calculate the BDEs of $CH_3C(O)O-H$ and $PhC(O)O-H$ to be 106.4 and 105.4 kcal/mol, respectively. Using eq 9, we can also estimate the standard reduction potential of the $CH_3C(O)O\bullet$ and $PhC(O)O\bullet$ radicals. A summary of these values is given in Table 1.

The general trend is that acetyl S−H bonds are weaker than acetyl O−H bonds by ca. 17 kcal/mol. It is also seen that a substitution of the methyl group for a phenyl in acetic acid and thiol acetic acid has very little effect on the S−H and O−H bond strengths. The somewhat higher BDE (ca. 1 kcal/mol) in the acetyl O−H or S−H bonds is mainly due to a slightly higher polarity of the bonds, which is reflected by the differences of the pK_a values.

The interesting finding that the kinetics of β-fragmentation of the $CH_3C(O)S\bullet$ radical is rather similar to that of the $PhC(O)S\bullet$ radical deserves special attention and will be discussed further. In Table 2, we summarized the experimental Arrhenius equations and the enthalpy changes ($\Delta H°_{\beta\text{-frag}}$) for the β-fragmentation of acetylthiyl, benzoylthiyl, acetyloxyl, and benzoyloxyl radicals.

The thermochemical data for the thiol acids are scarce. The value for $\Delta H°_f(CH_3C(O)SH)$ was measured to be −41.9 kcal/mol.[26] From our experimental value of the S−H bond enthalpy of 88.6 kcal/mol, we calculate $\Delta H°_f(CH_3C(O)S\bullet)$ to be −5.4 kcal/mol, using the value of $\Delta H°_f(H\bullet) = 52.1$ kcal/mol. The experimental values of $\Delta H°_f(PhC(O)SH)$ and $\Delta H°_f(PhC(O)S\bullet)$ are, to our knowledge, not known. A reasonable assumption is that the $\Delta H°_{\beta\text{-frag}}$ for the $PhC(O)S\bullet$ radical should be higher than that of the $CH_3C(O)S\bullet$ radical, since the activation energy of reaction 2 is higher (Evans−Polanyi relation[27]). The upper limit of the $\Delta H°_{\beta\text{-frag}}$ should be the activation energy of reaction 2. Given the upper and lower limits of the $\Delta H°_{\beta\text{-frag}}$, we can calculate the range in which $\Delta H°_f(PhC(O)SH)$ and $\Delta H°_f(PhC(O)S\bullet)$ are located, as shown in Table 2. The estimated value for the $\Delta H°_{\beta\text{-frag}}$ of reaction 3 should be (8.2 ± 2) kcal/mol according to the Evans−Polanyi relation. Thus further estimate of $\Delta H°_f(PhC(O)SH)$ and $\Delta H°_f(PhC(O)S\bullet)$ give the values (2.3 ± 2) and (37.6 ± 2) kcal/mol, respectively. For the $CH_3C(O)O\bullet$ and $PhC(O)O\bullet$ radicals, the $\Delta H°_{\beta\text{-frag}}$ values are calculated to be (−9.0 ± 1) and (1.9 ± 1) kcal/mol, respectively.

From a survey of Table 2, it is seen that the preexponential factors in the three measured Arrhenius equations are almost the same, indicating simple bond cleavage reactions with similar transition states. The $\Delta H°_{\beta\text{-frag}}$ for the $CH_3C(O)S\bullet$ and $PhC(O)S\bullet$ radicals are rather close to each other with both reactions being endothermic by ca. 7−8 kcal/mol. In contrast, the β-fragmentation reaction of the $CH_3C(O)O\bullet$ radical has an overall exothermicity of 9 kcal/mol and an extremely high rate, while that of the $PhC(O)O\bullet$ radical is endothermic by 1.9 kcal/mol. The difference of $\Delta H°_{\beta\text{-frag}}$ when substituting a methyl for a phenyl in an acetyloxyl radical is as large as 11 kcal/mol.

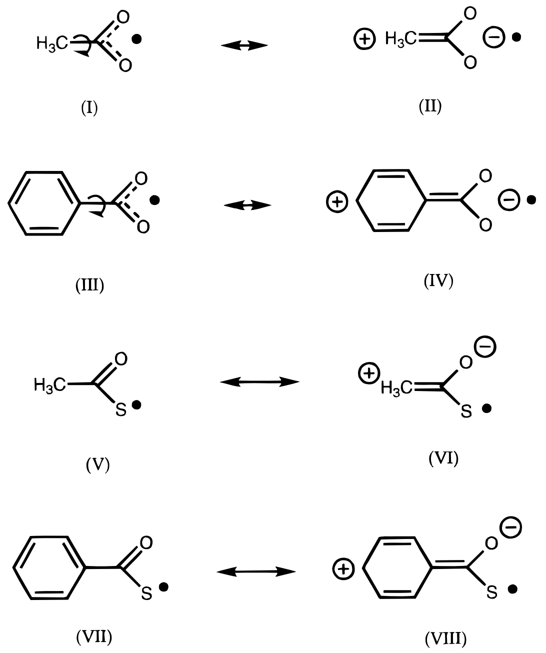
To be able to understand this apparent discrepancy, some related C−C bond energies were examined. The C−C bond energies in $Ph-CH_3$, CH_3-CH_3, and $Ph-Ph$ are 101.7, 89.9, and 114.5 kcal/mol, respectively.[26] The difference of the C−C bond energy in $Ph-CH_3$ as compared to that in CH_3-CH_3 is 11.8 kcal/mol. In terms of radical stabilization energy,[28,29] the difference between half of the BDEs of a symmetrical and nonpolar C−C bond in $Ph-Ph$ and the one in CH_3-CH_3 is 12.3 kcal/mol, i.e., the difference in stability of the methyl versus phenyl radicals. Thus, the 11 kcal/mol higher C−C bond energy of $PhC(O)O\bullet$ as compared to that of the $CH_3C(O)O\bullet$ radical is mainly attributable to the difference in the stability of the methyl vs phenyl radicals. It also indicates that there is only little interaction between the carbonyl group and the aromatic ring through the C−C bond. The rather similar C−C bond energies in $CH_3-C(O)S\bullet$ and $Ph-C(O)S\bullet$ radicals thus indicate that there is strong interaction between the carbonyl group and the methyl group or the aromatic ring. This is illustrated in Chart 1, where the possible radical canonical structures are shown. In structures **I** and **III**, the electron-withdrawing character of the carbonyl groups in $CH_3C(O)O\bullet$ and $PhC(O)O\bullet$ is “diluted” due to the

TABLE 2: Summary of the Arrhenius Parameters and the Enthalpy Change for the β-Fragmentation Reaction of Acylthiyl and Acyloxyl Radicals, along with the Corresponding Standard Enthalpy of Formation of the Radicals and the Acids in the Gas Phase[a]

no.	radical L β-fragmentation	Arrhenius parameter[b]	$\Delta H^\circ_f(L\bullet)$	$\Delta H^\circ_f(LH)$	$\Delta H^\circ_{\beta\text{-frag}}$[i]
(4)	$CH_3C(O)S\bullet \rightarrow CH_3\bullet + COS$	$\log k = (12.3 \pm 0.1) - (10.1 \pm 0.2)/\theta$[c]	-5.4[c]	-41.9[h]	7.3 ± 0.2
(3)	$PhC(O)S\bullet \rightarrow Ph\bullet + COS$	$\log k = (12.3 \pm 0.1) - (11.4 \pm 0.2)/\theta$[d]	(34.4) ~38.5[c]	(−0.9) ~3.2[c]	7.3 <(11.4)
			37.6 ± 2[j]	2.3 ± 2[j]	8.2 ± 2[j]
(1)	$CH_3C(O)O\bullet \rightarrow CH_3\bullet + CO_2$		-49.5[f]	-103.8[h]	-9.0 ± 1
(2)	$PhC(O)O\bullet \rightarrow Ph\bullet + CO_2$	$\log k = (12.6 \pm 0.1) - (8.6 \pm 0.3)/\theta$[e]	-17[g]	-70.3[h]	1.9 ± 1

[a] All unites in kcal/mol. [b] Rate constant k in s^{-1}; $\theta = 2.3RT$ kcal/mol. [c] This work. [d] Reference 12. [e] In pure CCl_4, from ref 10. [f] Reference 21. [g] Reference 22. [h] Reference 24. [i] Calculated by using the $\Delta H^\circ_f(CH_3\bullet) = 35 \pm 0.1$; $\Delta H^\circ_f(Ph\bullet) = 78.9 \pm 0.8$; $\Delta H^\circ_f(H\bullet) = 52.1$; $\Delta H^\circ_f(CO_2) = -94.05$; $\Delta H^\circ_f(COS) = -33.1$, from ref 24. [j] Estimated according to Evans−Polanyi relation.

CHART 1: Structures of $CH_3C(O)O\bullet$, $PhC(O)O\bullet$, $CH_3C(O)S\bullet$, and $PhC(O)S\bullet$ Radicals



resonance hybridization of the two oxygens. Furthermore, the symmetrical character of the C(O)O• moieties in the $CH_3C(O)O\bullet$ and PhC(O)O• radicals allows easy rotation of the C−C bonds, which hinders the group interaction through the bonds. Thus, the canonical structures **II** and **IV** are less important. This agrees with the experimental evidence that the lifetime of the PhC(O)O• radical is longer by ca. 23% in CCl_4 than in CH_3CN.[12] In the $CH_3C(O)S\bullet$ and PhC(O)S• radicals, where one oxygen in the carbonyloxyl groups is replaced by a sulfur, the symmetry is lost. The rotation of the C−C bonds becomes difficult as the radicals are mainly localized on the large sulfur atoms. As shown in Chart 1, the zwitterion structures of the $CH_3C(O)S\bullet$ **VI** and the PhC(O)S• **VIII** radicals become important due to the strong electron-withdrawing carbonyl group. The C−C bonds in the $CH_3-C(O)S\bullet$ and Ph−C(O)S• radicals have some double-bond character, which may strengthen the bonds and disguise the difference in stability between $CH_3\bullet$ and Ph• radicals.

Summary

One-electron oxidation of $CH_3C(O)S^-$ ions produces $CH_3C(O)S\bullet$ radicals. The reduction potentials $E^\circ(CH_3C(O)S\bullet/CH_3C(O)S^-)$ and $E^\circ(CH_3C(O)S\bullet,H^+/CH_3C(O)SH)$ were measured to be 1.22 and 1.42 V respectively, vs NHE. The $CH_3C(O)S\bullet$ radical subsequently undergoes β-fragmentation to form $CH_3\bullet$ and COS with a rate constant of $6.6 \times 10^4\ s^{-1}$ at room temperature. The β-fragmentation of the $CH_3C(O)S\bullet$ radical follows the Arrhenius equation, $\log(k_4/s^{-1}) = (12.3 \pm 0.1) - (10.1 \pm 0.2)/\theta$, where $\theta = 2.3RT$ kcal/mol. The experimental data for the kinetics and thermochemical properties of $CH_3C(O)SH$ and $CH_3C(O)S\bullet$ radicals obtained in this work are compared with those of the PhC(O)SH and PhC(O)S• radicals, along with their oxygen counterparts.

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