

# Communications

## Radical Substituent Effects of $\alpha$ -Sulfonium Groups

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Recently, sulfonium ylides have received increasing attention in synthetic organic chemistry because of their unique chiral epoxidation.<sup>1</sup> Deprotonation of the  $\alpha$ -C–H bonds next to the positively charged sulfur atom in sulfonium cations is well-known to be much easier than that next to the positively charged nitrogen atom in ammonium cations and to the positively charged phosphorus atom in phosphonium cations.<sup>2,3</sup> For example, the deuterium exchange of trimethylsulfonium cation was found to be  $2.0 \times 10^7$  and 11.6 times faster than those of tetramethylammonium and tetramethylphosphonium cations in the basic deuterioxide solution, respectively.<sup>3</sup> The equilibrium acidity of the *S*-phenacyldimethylsulfonium cation was reported to be about 1 p*K* unit stronger than that of *P*-phenacyltrimethylphosphonium cation.<sup>2b</sup> On the other hand, the quantitative information about the radical substituent effects of the  $\alpha$ -sulfonium groups is scarce in the literature. As far as we know, the only quantitative information for the  $\alpha$ -sulfonium groups is that reported for an  $\alpha$ -H<sub>2</sub>S<sup>+</sup> group as obtained from ab initio calculations.<sup>4</sup>

Theoretical calculations show that  $\alpha$ -H<sub>3</sub>N<sup>+</sup> and  $\alpha$ -H<sub>3</sub>P<sup>+</sup> groups are radical destabilizing.<sup>4</sup> This conclusion is in good agreement with the experimental results derived from the homolytic bond dissociation enthalpy (BDE) determination of the acidic C–H bond by a combination (eq 1) of the

$$\text{BDE}_{\text{HA}} = 1.37\text{p}K_{\text{HA}} + 23.1E_{\text{ox}}(\text{A}^-) + 73.3 \quad (1)$$

equilibrium acidity (p*K*<sub>HA</sub>) and the oxidation potential of the conjugate base [*E*<sub>ox</sub>(A<sup>−</sup>)].<sup>5</sup> For example, introduction of an  $\alpha$ -Me<sub>3</sub>N<sup>+</sup> group decreases the adjacent carbon radical stabilities by 2–5 kcal/mol,<sup>6</sup> and introduction of an  $\alpha$ -Ph<sub>3</sub>P<sup>+</sup> or an  $\alpha$ -(*n*-Bu)<sub>3</sub>P<sup>+</sup> group was found to decrease the adjacent

**Table 1. Equilibrium Acidities, Oxidation Potentials of the  $\alpha$ -Dialkylsulfonium Ylides, and the Homolytic Bond Dissociation Enthalpies (BDEs) of the Acidic C–H Bonds**

no.	substrate	p <i>K</i> <sub>HA</sub> <sup>a</sup>	<i>E</i> <sub>ox</sub> (A <sup>−</sup> ) <sup>d</sup>	BDE <sub>C–H</sub> <sup>e</sup>
1	PhCH <sub>3</sub>	~43 <sup>b</sup>		88–89 <sup>f</sup>
2	PhCH <sub>2</sub> <sup>+</sup> SMe <sub>2</sub>	17.8	−0.642	82.9
3	PhCH <sub>2</sub> <sup>+</sup> S( <i>n</i> -Bu) <sub>2</sub>	18.9	−0.667	83.8
4	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> <sup>+</sup> SMe <sub>2</sub>	18.4	−0.701	82.3
5	<i>p</i> -MeOCOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> <sup>+</sup> SMe <sub>2</sub>	14.6	−0.328	84.6
6	fluorene (FlH <sub>2</sub> )	22.6 <sup>c</sup>	−1.060 <sup>c</sup>	79.5
7	9-FlH <sup>+</sup> SMe <sub>2</sub>	6.5	−0.215	77.2

<sup>a</sup> Equilibrium acidities (in p*K* units) measured in DMSO solution by the overlapping indicator titration.<sup>9</sup> This study unless otherwise indicated. <sup>b</sup> Reference 9. <sup>c</sup> Reference 5a. <sup>d</sup> Irreversible oxidation potentials (in volts) measured in DMSO solution by a conventional cyclic voltammetry described previously and referenced to the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple.<sup>5a</sup> Irreversible oxidation potentials have been shown to agree within  $\pm 0.050$  V with the corresponding reversible oxidation potentials as obtained from fast-scan cyclic voltammetry.<sup>7b</sup> <sup>e</sup> BDEs (in kcal/mol) of the acidic C–H bonds as determined by using eq 1. <sup>f</sup> Reference 10.

carbon radical stabilities by 0–3 kcal/mol.<sup>7</sup> The C–H BDEs have generally been considered to provide the best reliable estimate for the quantitative stabilities of the carbon radicals formed by removal of one hydrogen atom.<sup>5,8</sup> In the present paper, we extend our studies to examine the radical substituent effects of the  $\alpha$ -sulfonium groups.

The equilibrium acidities and the oxidation potentials of the conjugate bases for five *S*-substituted dialkylsulfonium cations were determined in dimethyl sulfoxide (DMSO) solution by the methods described previously.<sup>5a</sup> The BDEs of the acidic C–H bonds in these sulfonium cations and related model compounds were calculated with eq 1,<sup>5</sup> and the results are summarized in Table 1.

The acidifying effects of the  $\alpha$ -Me<sub>3</sub>N<sup>+</sup> and  $\alpha$ -(*n*-Bu)<sub>3</sub>P<sup>+</sup> groups on the benzylic C–H bond of toluene were found to be 11.1 and 21.1 p*K* units, respectively.<sup>6,7</sup> Examination of the entries 2 and 3 in Table 1 shows that the acidifying effects of the  $\alpha$ -Me<sub>2</sub>S<sup>+</sup> and  $\alpha$ -(*n*-Bu)<sub>2</sub>S<sup>+</sup> groups on the benzylic C–H bond of toluene are 25.2 and 24.1 p*K* units, respectively. Note that the p*K* value of toluene was estimated to be about 43 in DMSO solution.<sup>9</sup> These results are in accord with the relative acidifying order of the  $\alpha$ -onium groups, i.e.,  $\alpha$ -sulfonium >  $\alpha$ -phosphonium  $\gg$   $\alpha$ -ammonium groups.<sup>2a–d</sup>

More interestingly, the benzylic C–H BDEs of the sulfonium cations PhCH<sub>2</sub><sup>+</sup>SMe<sub>2</sub> and PhCH<sub>2</sub><sup>+</sup>S(*n*-Bu)<sub>2</sub> were found to be 82.9 and 83.8 kcal/mol, respectively, indicating that introduction of an  $\alpha$ -Me<sub>2</sub>S<sup>+</sup> or an  $\alpha$ -(*n*-Bu)<sub>2</sub>S<sup>+</sup> group stabilizes the corresponding benzylic radicals by  $5 \pm 1$  kcal/mol since the benzylic C–H BDE of toluene is well-known to be in the range of 88–89 kcal/mol.<sup>10</sup> The  $\sim 5$  kcal/mol radical stabilizing effect of the  $\alpha$ -dialkylsulfonium groups is in sharp contrast to the radical destabilizing effect (−3.17 kcal/mol) reported for the  $\alpha$ -H<sub>2</sub>S<sup>+</sup> group from the ab initio calculations.<sup>4</sup>

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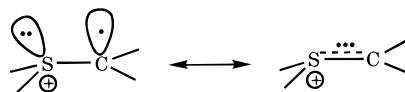
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To confirm the intriguing radical stabilizing effects of the  $\alpha$ -dialkylsulfonium groups, we have further synthesized two *S*-(para-substituted benzyl)dimethylsulfonium cations  $p\text{-GC}_6\text{H}_4\text{CH}_2^+\text{SMe}_2$  ( $G = \text{Me}$  and  $\text{COOMe}$ ). The related results are also included in Table 1 for comparison. As expected, introduction of an electron donating methyl group at the para position of the phenyl ring decreases the equilibrium acidity by 0.6 p*K* units, whereas introduction of an electron-withdrawing group ( $\text{COOMe}$ ) at the same place increases the equilibrium acidity by 3.2 p*K* units. Also, the equilibrium acidities of the three *S*-(para-substituted benzyl)dimethylsulfonium cations  $p\text{-GC}_6\text{H}_4\text{CH}_2^+\text{SMe}_2$  ( $G = \text{Me}$ ,  $\text{H}$ , and  $\text{COOMe}$ ) were found to be well correlated with the Hammett  $\sigma^-$  constants<sup>11</sup> with a slope of 4.2 p*K* units ( $R^2 = 0.999$ ). It is not surprising to find that the slope for the *S*-(para-substituted benzyl)dimethylsulfonium cations is similar to those observed for *P*-(para-substituted benzyl)triphenylphosphonium and *P*-(para-substituted benzyl)tri(*n*-butyl)phosphonium cations.<sup>7</sup> Examination of entries 4 and 5 in Table 1 also reveals that introduction of an  $\alpha\text{-Me}_2\text{S}^+$  group into the para-substituted toluenes decreases the benzylic C–H BDEs by  $5 \pm 1$  kcal/mol. Introduction of a para substituent is known to have negligible effects on the benzylic C–H BDEs.<sup>12</sup> Furthermore, introduction of an  $\alpha\text{-Me}_2\text{S}^+$  group into the 9-position of fluorene (entry 7, Table 1) was also found to decrease the acidic 9-C–H BDE by about 2 kcal/mol. The relatively smaller effects for the 9-C–H bond of fluorene is presumably due to the saturation effects.<sup>13</sup> These results lead us to conclude that the  $\alpha$ -sulfonium groups are *radical stabilizing* rather than *radical destabilizing* as predicted from the theoretical calculations.<sup>4</sup>

The radical-stabilizing effects of the  $\alpha$ -dialkylsulfonium ( $\alpha\text{-R}_2\text{S}^+$ ) groups are clearly associated with the free lone pair

Scheme 1



electrons of the sulfur atom in the sulfonium groups, which can form a two-center three-electron bond with the unpaired electron of the radical as shown in Scheme 1. This type of radical stabilization has been suggested to account for the significantly enhanced captodative radical-stabilizing effects.<sup>14</sup> Apparently, such radical-stabilizing interaction does not exist for the radical cations derived from the ammonium and phosphonium ylides due to the lack of the free lone-pair electrons of the nitrogen and phosphorus atoms in the corresponding onium radical cations.

The radical-stabilizing effects (RSEs) of the  $\alpha$ -dialkylsulfonium groups ( $\alpha\text{-R}_2\text{S}^+$ ) are smaller than those for the related  $\alpha\text{-RS}$  groups.<sup>8,15</sup> The relatively smaller radical-stabilizing effects of the  $\alpha$ -dialkylsulfonium groups can be attributed to the radical-destabilizing nature of the field/inductive effects of the positive charges on the sulfur atom.<sup>6,7</sup> The relative larger steric hindrance of the  $\alpha\text{-R}_2\text{S}^+$  compared to the  $\alpha\text{-RS}$  group may also partially contribute to the smaller radical stabilizing effects of the  $\alpha$ -dialkylsulfonium groups.<sup>16</sup>

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