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Effects of α-Ammonium, α-Phosphonium, and α-Sulfonium Groups on C−H Bond Dissociation Energies

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Abstract: C−H bond dissociation energies of α-ammonium-, α-phosphonium-, or α-sulfonium-substituted methanes and toluenes were calculated to a precision of 1−2 kcal/mol. It was found that α-ammonium, α-phosphonium, and α-sulfonium groups all destabilize a methyl radical. α-Ammonium also destabilizes a benzyl radical, whereas α-phosphonium and α-sulfonium either slightly stabilize or destabilize a benzyl radical depending on their alkylation state.

The effect of substituents on the stability of carbon radicals is important in understanding the organic reactions involving radicals as reactants, intermediates, or products.[1] A measure of the substituent effect on carbon radical stability is provided by the C−H homolytic bond dissociation energies (BDE).[2] If the C−H BDE of a substituted compound is larger (or smaller) than that of the unsubstituted case, the substituent is considered to destabilize (or stabilize) the carbon radical.

Recently, Radom proposed that an α-substituent affects the stability of methyl radicals in four general ways.[3] (1) π-Acceptors stabilize methyl radicals as they delocalize the odd electron into their π-systems. (2) Lone pair donors stabilize methyl radicals through a three-electron interaction between a lone pair on the substituent and the odd electron on the radical. (3) Alkyl groups stabilize methyl radicals via hyperconjugation. (4) Polyfluoroalkyl groups destabilize methyl radicals by inductively withdrawing electron density from the electron-deficient radical center.

Quaternary ammonium groups are also inductive electron acceptors. They have little ability to delocalize an adjacent odd electron via hypercojugation. Therefore, quaternary ammoniums should destabilize a methyl radical. This prediction is consistent with the experimental data of Bordwell et al. They found that introduction of an α-Me_3N^+ group increases the C−H BDE of toluene by 2−5 kcal/mol.[4] They also reported that introduction of α-Ph_3P^+ increases the C−H BDE of toluene by 0−3 kcal/mol.[5] However, using Bordwell's method, it was found recently that α-sulfonium groups stabilize carbon radicals by 4−6 kcal/mol.[6] This result is contradictory to an earlier theoretical prediction at the HF/4-31g(d) level.[7]

The contradiction may arise from the solvation effect. According to the Bordwell's method, the BDE was determined using the following empirical equation.[8]

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

In eq 1, pK_{HA} is the equilibrium acidity for the C−H bond and $E_{\mathrm{ox}}(\mathrm{A}^-)$ is the oxidation potential of the conjugate base A^-.[9] The empirical constant, 73.3, was determined from the C−H BDEs of many nonpolar compounds, whose homolysis probably causes little solvation energy change. However, for some highly polar compounds whose homolysis may cause considerable solvation energy variation, the use of the same empirical constant (73.3) may lead to inaccurate BDEs.

Since ammonium-, phosphonium-, or sulfonium-substituted compounds are highly polar, their BDEs measured using eq 1 might be inaccurate. Thus, a reexamination of the experimental BDEs of these compounds is necessary. Since currently the composite ab initio methods can predict the BDEs to a precision of 1−2 kcal/mol,[3] we conducted composite ab initio calculations to reevaluate the substituent effects of α-ammonium, phosphonium, or sulfonium groups on carbon radical stability.

Methods. All calculations were conducted using Gaussian 98.[10] Geometry optimization was done using UB3LYP/6-31+g* except for the composite ab initio calculations. For each species, all the possible conformations were examined to find the lowest-energy structure. All the optimized structures were confirmed to be real minima without any imaginary frequency.

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TABLE 1. Theoretical C−H BDEs (kcal/mol) Associated with Methyl Radicals

method	UB3LYP/ 6-31+g(d)	UB3LYP/ 6-311++g(3d,3p)	RMP2/ 6-311++g(2d,p)	UCCSD(T)/ 6-311++g(d,p)	UQCISD(T)/ 6-311++g(d,p)	CBS-4M	CBS-Q	G3
CH_4	104.5	105.5	101.0	101.4	101.4	104.6	104.2	104.1
$H_3N^+{-}CH_3$	108.3	109.1	105.5	106.2	106.3	108.8	109.0	109.1
$CH_3{-}H_2N^+{-}CH_3$	107.1	107.9	104.9	105.5	105.5	108.1	107.6	107.8
$(CH_3)_2HN^+{-}CH_3$	106.9	107.8	104.8	105.3	105.4	107.9	108.0	108.1
$(CH_3)_3N^+{-}CH_3$	106.1	107.1	104.6			107.5	107.6	107.8
$H_3P^+{-}CH_3$	104.8	106.0	102.8	103.0	103.0	106.0	105.5	105.6
$CH_3{-}H_2P^+{-}CH_3$	104.0	105.3	102.3	102.5	102.5	105.4	104.8	105.0
$(CH_3)_2HP^+{-}CH_3$	103.5	104.7	102.0	102.0	102.0	105.1	104.8	104.6
$(CH_3)_3P^+{-}CH_3$	103.2	105.0	101.9	-	-	104.8	104.4	104.4
$H_2S^+{-}CH_3$	106.9	107.6	104.6	104.7	104.7	106.9	107.1	107.2
$CH_3{-}HS^+{-}CH_3$	105.0	106.0	103.6	103.5	103.5	106.0	105.3	105.7
$(CH_3)_2S^+{-}CH_3$	104.1	104.9	102.7	102.7	102.6	104.7	104.6	104.9

[a] All geometries were optimized at the UB3LYP/6-31+g(d) level except for the G3, CBS-Q, and CBS-4M calculations.

TABLE 2. Theoretical and Experimental BDEs (kcal/mol) Associated with Benzyl Radicals

compounds	experimental	RMP2/ 6-311++g(d,p)	CBS-4M
Ph-CH_3	88−89[b]	88.7	89.1
$H_3N^+{-}CH_2{-}Ph$		93.7	93.7
$CH_3{-}H_2N^+{-}CH_2{-}Ph$		93.2	93.1
$(CH_3)_2HN^+{-}CH_2{-}Ph$		93.0	92.3
$(CH_3)_3N^+{-}CH_2{-}Ph$	90.5[c]	96.6	96.7
$H_3P^+{-}CH_2{-}Ph$		86.9	87.0
$CH_3{-}H_2P^+{-}CH_2{-}Ph$		87.2	87.4
$(CH_3)_2HP^+{-}CH_2{-}Ph$		88.1	88.0
$(CH_3)_3P^+{-}CH_2{-}Ph$		89.6	89.7
$H_2S^+{-}CH_2{-}Ph$		89.0	89.7
$CH_3{-}HS^+{-}CH_2{-}Ph$		89.4	88.6
$(CH_3)_2S^+{-}CH_2{-}Ph$	82.9[d]	88.5	88.5

[a] All geometries were optimized at the UB3LYP/6-31+g(d) level except for the CBS-4M calculations. [b] Taken from ref 2. [c] Taken from ref 5. [d] Taken from ref 8.

Single-point energies were calculated at UB3LYP/6-31+g(d), UB3LYP/ 6-311++g(3d,3p), RMP2/6-311++g(d,p), UCCSD(T)/6-311++g(d,p), and UQCISD(T)/6-311++g(d,p) levels. The standard G3, CBS-Q, and CBS-4M methods were also used. The BDE is calculated as the enthalpy change of the following reaction at 298 K in a vacuum.

$$\mathrm{RCH_2\text{-}H} \rightarrow \mathrm{RCH_2}\bullet + \mathrm{H}\bullet \qquad (2)$$

The enthalpy of formation for each species was calculated using eq 3.

$$H_{298} = E + ZPE + \Delta H_{298-0} \qquad (3)$$

Herein, the zero-point energy (ZPE) was calculated at the UB3LYP/6-31+g(d) level (unscaled). ΔH_{298-0} is the standard temperature correction term.

BDEs of Substituted Methanes. In Table 1 are summarized the C−H BDEs of methane and its ammonium-, phosphonium-, and sulfonium-substituted derivatives calculated using different theoretical methods. The substituent effects on the C−H BDEs of methane calculated using G3 are also shown in Figure 1.

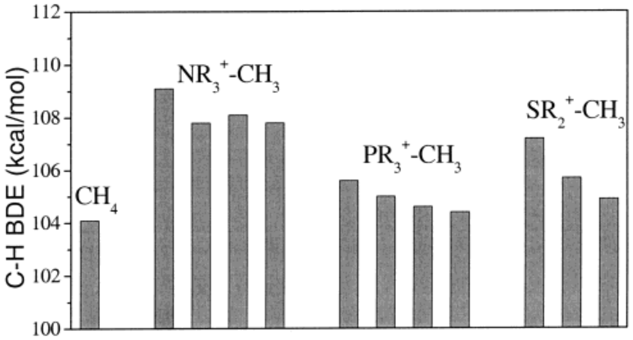

FIGURE 1. Substituent effects on the C−H BDE of methane calculated using G3.

According to CBS-4M, CBS-Q, and G3 results, the C−H BDE of CH_4 is 104−105 kcal/mol. This value is in good agreement with the recommended experimental value, 104.9 ± 0.1 kcal/mol.[2] UB3LYP/6-31+g(d) and UB3LYP/6-311++g(3d,3p) provide 104.5 and 105.5 kcal/mol, which are also close to the experimental result. In comparison, RMP2/6-311++g(2d,p), UCCSD(T)/6-311++g-(d,p), and UQCISD(T)/6-311++g(d,p) underestimate the C−H BDE of methane by 3−4 kcal/mol.[11]

According to all the theoretical methods the NH_3^+ substitution increases the C−H BDE of methane by 4−5 kcal/mol. Therefore, NH_3^+ destabilizes the methyl radical as previously proposed. $CH_3NH_2^+$, $(CH_3)_2NH^+$, and $(CH_3)_3N^+$ substitutions also increase the C−H BDE of methane, but to a lesser extent than NH_3^+. For $(CH_3)_3N^+$, G3 predicts the destabilization energy to be 3.7 kcal/mol, compared to 3.4, 2.9, and 3.6 kcal/mol predicted by CBS-Q, CBS-4M, and RMP2/6-311++g(2d,p), respectively. The UB3LYP methods predict a destabilization energy of 1.6 kcal/mol for $(CH_3)_3N^+$. It appears that the UB3LYP methods underestimate the destabilization effect of the ammonium groups.

PH_3^+ increases the C−H BDE of methane by about 1.5 kcal/mol according to RMP2, UCCSD(T), UQCISD(T), CBS-4M, CBS-Q, and G3. The UB3LYP methods predict a smaller increase, i.e., 0.3−0.5 kcal/mol. Therefore, UB3LYP also underestimates the destabilization effect

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[11] We used a number of different theoretical methods in order to make sure that the observed substituent effects are independent of the calculation method. For more details, please read: (a) Song, K.-S.; Cheng, Y.-H.; Fu, Y.; Liu, L.; Li, X.-S.; Guo, Q.-X. *J. Phys. Chem. A* **2002**, *106*, 6651. (b) Cheng, Y.-H.; Liu, L.; Song, K.-S.; Guo, Q.-X. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1406. (c) Fu, Y.; Mou, Y.; Lin, B.-L.; Liu, L.; Guo, Q.-X. *J. Phys. Chem. A* **2002**, *106*, 12386. (d) Feng, Y.; Huang, H.; Liu, L.; Guo, Q.-X. *Phys. Chem. Chem. Phys.* **2003**, *5*, 685.

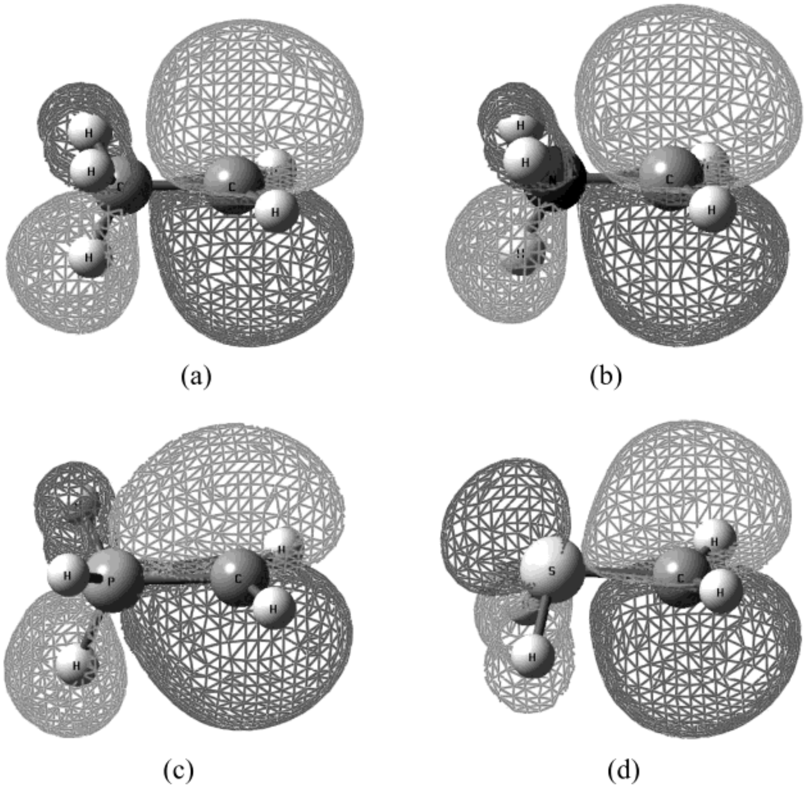

FIGURE 2. SOMO of (a) $CH_3CH_2\bullet$, (b) $H_3N^+CH_2\bullet$, (c) $H_3P^+CH_2\bullet$, and (d) $H_2S^+CH_2\bullet$ radicals.

of the phosphoniums. $CH_3PH_2^+$, $(CH_3)_2PH^+$, and $(CH_3)_3P^+$ increase the C−H BDE of methane, but to a lesser extent than PH_3^+. For $(CH_3)_3P^+$, CBS-4M, CBS-Q, and G3 predict the destabilization effect to be 0.2−0.3 kcal/mol.

According to all the theoretical results, SH_2^+ increases the C−H BDE of methane by about 2−3 kcal/mol. Therefore, SH_2^+ is a destabilizing substituent for the methyl radical. The earlier theoretical prediction using the HF/4-31g(d) method is correct.[7] CH_3SH^+ and $(CH_3)_2S^+$ also increase the C−H BDE of methane, but to a lesser extent than SH_2^+. For $(CH_3)_2S^+$, CBS-4M, CBS-Q, and G3 predict destabilization energies of 0.1, 0.4, and 0.8 kcal/mol, respectively, which are smaller than predictions by RMP2 (1.6 kcal/mol), UCCSD(T) (1.3 kcal/mol), and UQCISD(T) (1.2 kcal/mol). However, UB3LYP predicts that $(CH_3)_2S^+$ stabilizes the methyl radical by 0.4−0.6 kcal/mol. According to the results for ammonium and phosphonium, we consider the UB3LYP results for $(CH_3)_2S^+$ to be incorrect.

Thus, ammonium, phosphonium, and sulfonium are all destabilizing groups for the methyl radical. The extent of the destabilization roughly decreases in the order ammonium > sulfonium > phosphonium.

BDEs of Substituted Toluenes. The C−H BDEs of substituted toluenes can only be calculated using RMP2 and CBS-4M.[12] According to these two methods, the C−H (benzylic) BDE of Ph-CH_3 is about 89 kcal/mol. This value is in good agreement with the recommended experimental value, 88−89 kcal/mol.[2]

Introduction of an α-NH_3^+ substituent increases the C−H BDE of toluene by 3−5 kcal/mol. $NH_2(CH_3)^+$ and $NH(CH_3)_2^+$ also increase the C−H BDE of toluene, but to a lesser extent than NH_3^+. However, $N(CH_3)_3^+$ increases the C−H BDE of toluene by 8 kcal/mol, which is larger than increases from NH_3^+, $NH_2(CH_3)^+$, and $NH(CH_3)_2^+$. This may be due to the steric effect (e.g., repulsion between N−CH_3 and C−H on the phenyl ring).

Introduction of an α-PH_3^+ substituent decreases the C−H BDE of toluene by 2 kcal/mol. $PH_2(CH_3)^+$ and $PH(CH_3)_2^+$ also decrease the C−H BDE of toluene, but to a lesser extent than PH_3^+. Nevertheless, $P(CH_3)_3^+$ increases the C−H BDE of toluene by 0.6−0.9 kcal/mol.

Introduction of an α-SH_2^+ substituent increases the C−H BDE of toluene by 0.3−0.6 kcal/mol. $SH(CH_3)^+$- and $S(CH_3)_2^+$-substituted toluenes have almost the same C−H BDE as toluene.

Thus, α-ammonium destabilizes the benzyl radical. α-Phosphonium and α-sulfonium may either slightly stabilize or destabilize the benzyl radical depending on their alkylation state.

For $(CH_3)_3N^+$−CH_2−Ph, the experimental C−H BDE is 90.5 kcal/mol.[5] This value is about 6 kcal/mol smaller than the theoretical prediction. For $(CH_3)_2S^+$−CH_2−Ph, the experimental C−H BDE is 82.9 kcal/mol.[8] This value is also about 6 kcal/mol smaller than the theoretical result. Therefore, the constant 73.3 in eq 1 is not applicable to the ammonium-, phosphonium-, and sulfonium-substituted compounds.

Origin of the Substituent Effects. In Figure 2 are shown the singly occupied molecular orbitals (SOMO) of the $CH_3CH_2\bullet$, $H_3N^+CH_2\bullet$, $H_3P^+CH_2\bullet$, and $H_2S^+CH_2\bullet$ radicals calculated using RMP2/6-311++g(2d,p).

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[12] We did not use the DFT method for the toluene systems because according to the results in Table 1, UB3LYP does not provide accurate substituent effects for the ammonium, phosphonium, and sulfonium groups.

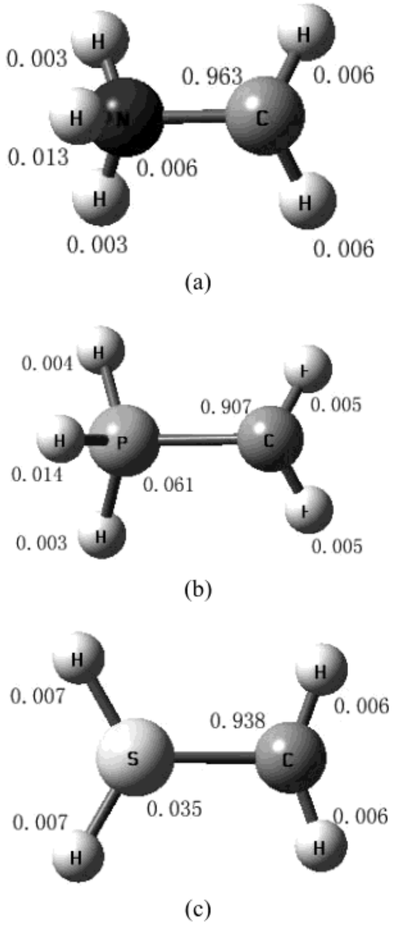

FIGURE 3. Spin distributions of (a) $H_3N^+CH_2\bullet$, (b) $H_3P^+CH_2\bullet$, and (c) $H_2S^+CH_2\bullet$ radicals calculated using the RMP2/6-311++g(2df,p) method.

According to Figure 2, the shape of the SOMOs of the four radicals is basically the same, i.e., a combination of the p orbital on carbon and the σ bonding orbital of the X−H bond (X = C, N, P, or S). Therefore, the hyperconjugation effect exists in all four radicals. The fact that CH_3 stabilizes the carbon radical whereas NH_3^+, PH_3^+, and SH_2^+ destabilize the carbon radical must be due to the strong inductively electron-withdrawing character of NH_3^+, PH_3^+, and SH_2^+. The extent of the destabilization decreases in the order ammonium > sulfonium > phosphonium because the electronegativity of N is larger than that of S and P.

It was proposed in the earlier study that the lone pair electrons on sulfonium could stabilize the carbon radical via a two-center, three-electron bond.[8] Since ammonium and phosphonium do not have any lone pair electrons, the substituent effects of sulfonium were proposed to be different from those of ammonium and phosphonium. However, from Figure 2, it can be seen that the sulfur atom in SH_2^+ is almost sp^3 hybridized. As a result, the lone pair electrons on S cannot be well conjugated with the odd electron of the carbon radical. Thus, the proposed two-center, three-electron bonding interaction is not significant.

The spin density distribution can also provide insight into the substituent effects on radical stability. As shown in Figure 3, the spins carried by the CH_2 moiety in H_3N^+-$CH_2\bullet$, $H_3P^+CH_2\bullet$, and $H_2S^+CH_2\bullet$ radicals are all close to unity. This means that H_3N^+, H_3P^+, and H_2S^+ can barely delocalize any odd electron carried by the carbon radical. The spin distribution of the $H_2S^+CH_2\bullet$ radical also confirms that the lone pair electrons on S cannot effectively form a two-center, three-electron bond.

Conclusions. According to the results of various theoretical methods, α-ammonium, α-phosphonium, and α-sulfonium groups all destabilize a methyl radical. α-Ammonium also destabilizes a benzyl radical, whereas α-phosphonium and α-sulfonium either slightly stabilize or destabilize a benzyl radical depending on their alkylation state. The origin of the radical destabilization effect is the inductive acceptor character of the ammonium, phosphonium, and sulfonium groups. These groups cannot effectively delocalize the odd electron on the carbon radical, but they can remove the electron density from the electron-deficient radical center.

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Supporting Information Available: Detailed descriptions of the optimized geometry, total energy, and enthalpy of each of the molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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