

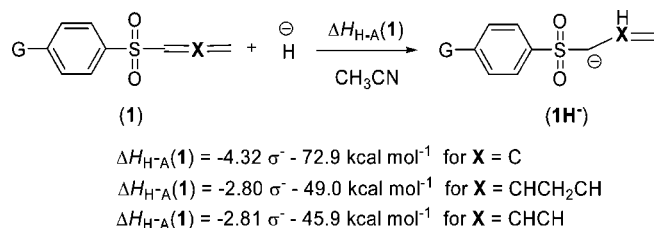
## Hydride Affinities of Cumulated, Isolated, and Conjugated Dienes in Acetonitrile

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The hydride affinities (defined as the enthalpy changes in this work) of 15 polarized dienes [five phenyl sulfone substituted allenes (**1a**), the corresponding five isolated dienes (**1b**), and the corresponding five conjugated dienes (**1c**)] in acetonitrile solution were determined by titration calorimetry for the first time. The results display that the hydride affinity scales of the 15 dienes in acetonitrile range from  $-71.6$  to  $-73.9$  kcal/mol for **1a**, from  $-46.2$  to  $-49.7$  kcal/mol for **1b**, and from  $-45.0$  to  $-46.5$  kcal/mol for **1c**, which indicates that the hydride-obtaining abilities of the cumulated dienes (**1a**) are not only much larger than those of the corresponding conjugated dienes (**1c**) but also much larger than those of the corresponding isolated dienes (**1b**). The hydrogen affinities of the 15 dienes as well as the hydrogen affinities and the proton affinities of the radical anions of the dienes (**1<sup>•-</sup>**) in acetonitrile were also evaluated by using relative thermodynamic cycles according to Hess's law. The results show that (i) the hydrogen affinities of the neutral dienes **1** cover a range from  $-44.5$  to  $-45.6$  kcal/mol for **1a**, from  $-20.4$  to  $-21.4$  kcal/mol for **1b**, and from  $-17.3$  to  $-18.5$  kcal/mol for **1c**; (ii) the hydrogen affinities of the radical anions of the dienes (**1<sup>•-</sup>**) in acetonitrile cover a range from  $-40.6$  to  $-47.2$  kcal/mol for **1a<sup>•-</sup>**, from  $-21.6$  to  $-29.6$  kcal/mol for **1b<sup>•-</sup>**, and from  $-10.0$  to  $-15.4$  kcal/mol for **1c<sup>•-</sup>**; (iii) the proton affinities of the 15 **1a<sup>•-</sup>** in acetonitrile cover a range from  $-97.0$  to  $-100.6$  kcal/mol for **1a<sup>•-</sup>**, from  $-77.8$  to  $-83.4$  kcal/mol for **1b<sup>•-</sup>**, and from  $-66.2$  to  $-68.9$  kcal/mol for **1c<sup>•-</sup>**. The main reasons for the great difference between the cumulated dienes and the corresponding isolated and conjugated dienes in the hydride affinity, hydrogen affinity, and proton affinity have been examined. It is evident that these experimental results should be quite valuable to facilitate the elucidation of the origins of the especially high chemical potencies of the allenes, the choice of suitable hydride reducing agents to reduce the dienes, and the analyses on the reduction mechanisms.

### Introduction

Allenes (cumulated dienes) are one class of very important dienes that have successive double bonds with no intervening single bonds.<sup>1</sup> Since allenes have two  $\pi$ -orbitals perpendicular to each other, allenes were considered to be highly unstable for a long period of time, which badly retarded the study of the chemistry of allenes. However, due to their extensive presence in natural products with interesting biological activities and their great potential applications as electrophilic agents in organic syntheses, allenes have received much more intense attention

in recent years than ever before.<sup>2-6</sup> Systematic examination of the past publications on the chemistry of allenes shows that although there are many chemists who have devoted much time to the study of allenes, the main attention was limited to the

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preparation, reactions, and applications of allenes.<sup>7–14</sup> Rather scant attention has been paid to the study of the fundamental thermodynamics of reactions of allenes by using experimental methods.<sup>15</sup> Since in the reactions of allenes, the most are all involved in electrophilic additions or reductions of the successive double bonds,<sup>16</sup> the hydride affinity of allenes should be the most intrinsic thermodynamic scale to measure their chemical

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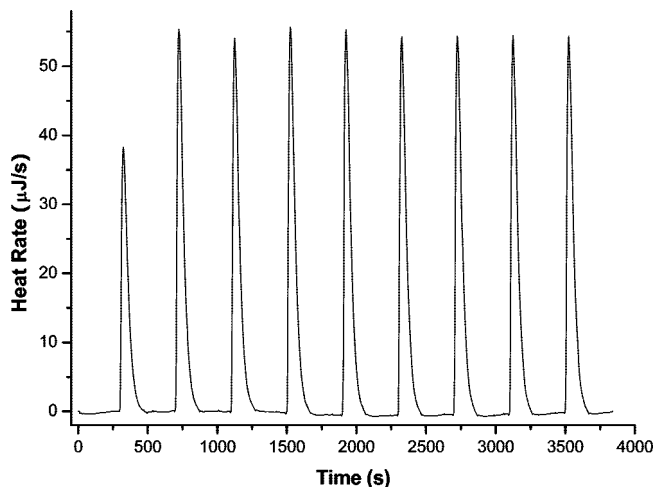
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**FIGURE 1.** Isothermal titration calorimetry (ITC) for the reaction heat of  $1aH^-$  ( $G = H$ ) with 9-phenylxanthylum cation ( $PhXn^+ClO_4^-$ ) in acetonitrile at 298 K. Titration was conducted by adding  $8 \mu L$  of  $PhXn^+ClO_4^-$  (3.86 mM) every 400 s into the acetonitrile containing the  $1aH^-$  ( $G = H$ ) (ca. 10.0 mM), which was obtained in situ from the reactions of the corresponding saturated neutral compounds ( $1aH_2$ ) with KH.

activities and reactivities. It is evident that the terrible lack of knowledge about the hydride affinity of allenes in solution must bring a lot of difficulties to understand the chemistry of allenes and to further develop the application of allenes. Several years ago we embarked on a major project to experimentally determine the hydride affinity scale of various unsaturated organic compounds in organic solvent.<sup>17</sup> Herein we wish to offer the hydride affinities of phenyl sulfone substituted allenes in acetonitrile as the first report about the hydride affinities of allenes in solution.

In addition to phenyl sulfone substituted allenes (**1a**), the corresponding isolated dienes (**1b**) and the corresponding conjugated dienes (**1c**) were also investigated in this work for a comparison to search the structural origins of allenes resulting in their special chemical reactivity.

## Results and Discussion

The hydride affinity of dienes (**1**) is defined in this work as the enthalpy change of the reaction of **1** with a free hydride ion in acetonitrile to form the corresponding carbanion  $1H^-$  at 298 K (eqs 1 and 2). Since the free hydride anion in acetonitrile is not available, it is clearly difficult to directly determine the hydride affinity of the allenes in acetonitrile by experimental methods. However, the hydride affinity of **1** in solution [ $\Delta H_{H-A}(1)$ ] can be easily obtained from the reaction enthalpy change of the corresponding carbanions  $1H^-$  with a strong hydride acceptor, such as 9-phenylxanthylum cation ( $PhXn^+$ ) (eqs 3 and 4). In eq 4,  $\Delta H_r$  is the enthalpy change of the reaction (eq 3) in acetonitrile, which can be determined by using titration calorimetry (Figure 1);  $\Delta H_{H-A}(PhXn^+)$  is the hydride affinity of  $PhXn^+$  in acetonitrile ( $-96.8 \text{ kcal mol}^{-1}$ ), which can be

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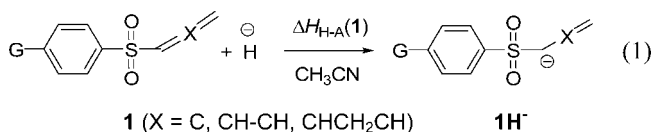
(18)  $1H^-$  was prepared by deprotonation of the parent compound  $1H_2$  with KH in acetonitrile. Reaction of  $1H^-$  with  $PhXn^+$  in acetonitrile gives the corresponding dienes **1** and  $PhXnH$  quantitatively by hydride transfer, which were identified by MS and  $^1H$  NMR spectroscopy. Since the hydride transfer from  $1H^-$  to  $PhXn^+$  in acetonitrile is not only fast but also quantitative, the reaction enthalpy change  $\Delta H_r$  can be directly determined by titration calorimetry.

**TABLE 1.** Reaction Enthalpy Changes of Carbanion  $\mathbf{1H}^-$  with 9-Phenylxanthylum ( $\text{PhXn}^+$ ) and Redox Potentials of  $\mathbf{1}$  and  $\mathbf{1H}^-$  in Acetonitrile at 298 K

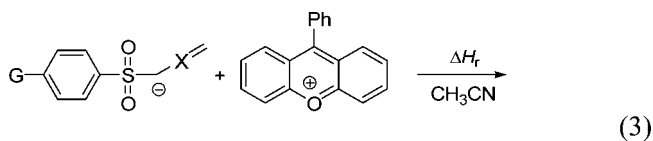
<b>1</b>	$\Delta H_r^a$	$E(\mathbf{1H}^{0-})^b$		$E(\mathbf{1}^{0-})^b$	
		CV	OSWV	CV	OSWV
<b>1a (X = C)</b>					
$\text{CH}_3\text{O}$	-25.2	0.030	0.005	-2.424	-2.393
$\text{CH}_3$	-24.5	0.051	0.031	-2.365	-2.334
H	-23.7	0.097	0.057	-2.315	-2.284
Cl	-23.1	0.156	0.129	-2.251	-2.221
Br	-22.9	0.164	0.135	-2.168	-2.137
<b>1b (X = <math>\text{CHCH}_2\text{CH}</math>)</b>					
$\text{CH}_3\text{O}$	-48.6	0.057	0.025	-2.705	-2.663
$\text{CH}_3$	-48.2	0.074	0.044	-2.646	-2.602
H	-47.7	0.100	0.078	-2.538	-2.506
Cl	-47.3	0.159	0.120	-2.404	-2.366
Br	-47.1	0.167	0.135	-2.392	-2.360
<b>1c (X = <math>\text{CHCH}</math>)</b>					
$\text{CH}_3\text{O}$	-51.8	0.043	0.013	-2.199	-2.172
$\text{CH}_3$	-51.3	0.064	0.035	-2.161	-2.137
H	-50.9	0.090	0.059	-2.113	-2.086
Cl	-50.4	0.155	0.122	-2.068	-2.045
Br	-50.3	0.161	0.130	-2.020	-1.990

<sup>a</sup>  $\Delta H_r$  obtained from the reaction heats of eq 3 by switching the sign; the latter were measured by titration calorimetry in acetonitrile at 298 K. The data, given in  $\text{kcal mol}^{-1}$ , are average values of at least three independent runs. The reproducibility is  $\pm 0.5 \text{ kcal mol}^{-1}$ . <sup>b</sup> Measured by CV and OSWV methods in acetonitrile at 298 K, the unit in volts vs  $\text{Fc}^+/\text{Fc}^0$  and reproducible to 5 mV or better.

obtained from the reaction heat of  $\text{PhXn}^+$  with 1-benzyl-1,4-dihydronicotinamide (BNAH) in acetonitrile ( $32.6 \text{ kcal mol}^{-1}$ ).<sup>19</sup> The enthalpy changes of the reactions of  $\mathbf{1H}^-$  with  $\text{PhXn}^+$  (eq 3) are listed in Table 1. The detailed hydride affinities of the three types of dienes, **1a–1c**, in acetonitrile are summarized in Table 2.



$$\Delta H_{\text{H-A}}(\mathbf{1}) = H_f(\mathbf{1H}^-) - [H_f(\text{H}^-) + H_f(\mathbf{1})] \quad (2)$$



$$\Delta H_{\text{H-A}}(\mathbf{1}) = \Delta H_{\text{H-A}}(\text{PhXn}^+) - \Delta H_r \quad (4)$$

As the reductions of dienes by hydride anion could involve multistep hydride transfer mechanism in addition to the one-step hydride transfer pathway (Scheme 1), it is evident that the hydrogen affinity of **1**,  $\Delta H_{\text{HA}}(\mathbf{1})$ , as well as the proton affinity and the hydrogen affinity of the corresponding radical carbanion

(19) Hydride affinity of  $\text{PhXn}^+$  in acetonitrile is equal to the reaction enthalpy change of BNAH with  $\text{PhXn}^+$  in acetonitrile ( $32.6 \text{ kcal mol}^{-1}$  determined in this work) minus the C<sub>4</sub>-H bond heterolytic dissociation energy of BNAH in acetonitrile, the latter can be available from our previous work ( $64.2 \text{ kcal mol}^{-1}$ ).<sup>22</sup>

**TABLE 2.** Hydride and Hydrogen Affinities of Dienes (**1**), as well as Proton Affinities and Hydrogen Affinities of Radical Anions of the Dienes ( $\mathbf{1}^-$ ) in Acetonitrile ( $\text{kcal mol}^{-1}$ )<sup>a</sup>

dinene ( <b>1</b> )	$\Delta H_{\text{H-A}}(\mathbf{1})^b$	$\Delta H_{\text{HA}}(\mathbf{1}^-)^c$	$\Delta H_{\text{PA}}(\mathbf{1}^-)^c$	$\Delta H_{\text{HA}}(\mathbf{1}^-)^c$
<b>1a (X = C)</b>				
$\text{CH}_3\text{O}$	-71.6	-45.3	-47.2	-100.6
$\text{CH}_3$	-72.3	-45.4	-46.0	-99.9
H	-73.1	-45.6	-45.0	-99.5
Cl	-73.7	-44.5	-42.5	-98.7
Br	-73.9	-44.6	-40.6	-97.0
<b>1b (X = <math>\text{CHCH}_2\text{CH}</math>)</b>				
$\text{CH}_3\text{O}$	-48.2	-21.4	-29.6	-83.4
$\text{CH}_3$	-48.6	-21.4	-28.2	-82.4
H	-49.1	-21.1	-25.7	-80.7
Cl	-49.5	-20.5	-21.9	-77.8
Br	-49.7	-20.4	-21.6	-77.9
<b>1c (X = <math>\text{CHCH}</math>)</b>				
$\text{CH}_3\text{O}$	-45.0	-18.5	-15.4	-68.9
$\text{CH}_3$	-45.5	-18.5	-14.6	-68.6
H	-45.9	-18.3	-13.2	-67.8
Cl	-46.4	-17.4	-11.3	-67.3
Br	-46.5	-17.3	-10.0	-66.2

<sup>a</sup> Relative uncertainties were estimated to be smaller than or close to  $1 \text{ kcal mol}^{-1}$  in each case. <sup>b</sup>  $\Delta H_{\text{H-A}}(\mathbf{1})$  was estimated from eq 4, taking  $\Delta H_{\text{H-A}}(\text{PhXn}^+) = -96.8 \text{ kcal mol}^{-1}$ . <sup>c</sup> Estimated from eqs 5–7, respectively, taking  $E^\circ(\text{H}^{0-}) = -1.137 \text{ V vs Fc}^+/\text{Fc}^0$ ,  $E^\circ(\text{H}^{+0}) = -2.307 \text{ V vs Fc}^+/\text{Fc}^0$  ( $\text{Fc} = \text{ferrocene}$ )<sup>21</sup> and choosing the redox potentials of **1** and  $\mathbf{1H}^-$  measured by OSWV method (Table 1) as  $E^\circ(\mathbf{1}^{0-})$  and  $E^\circ(\mathbf{1H}^{0-})$ , because OSWV has been verified to be more reliable method to evaluate the standard one-electron redox potentials of analyte with irreversible electrochemical process than CV in our previous work.<sup>22</sup>

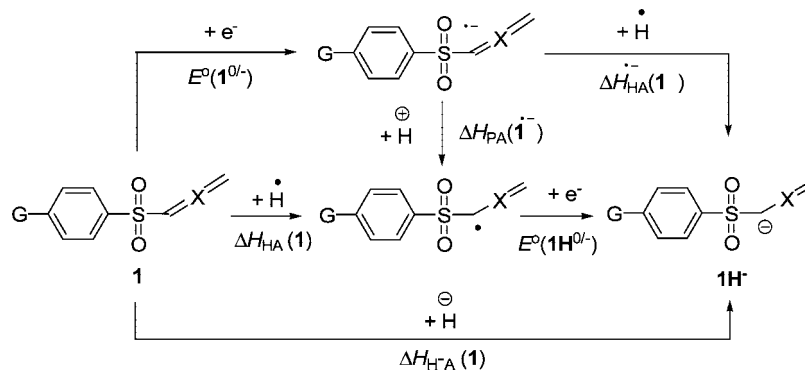
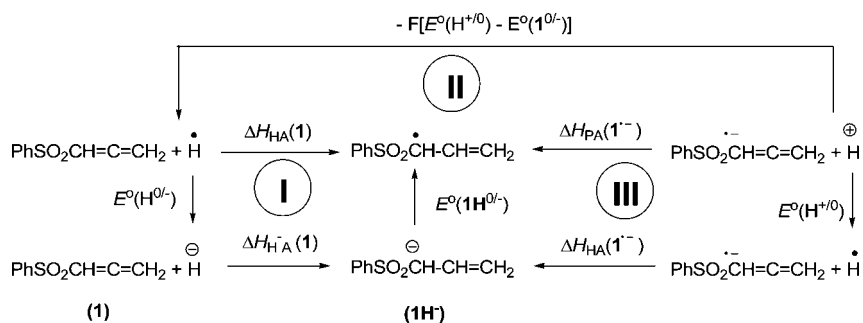
( $\mathbf{1}^-$ ),  $\Delta H_{\text{PA}}(\mathbf{1}^-)$ , and  $\Delta H_{\text{HA}}(\mathbf{1}^-)$  are also of paramount importance in elucidation of the reduction mechanism of dienes and prediction of the chemical properties of the various reaction intermediates of the dienes. In this work, the hydrogen affinity of **1** as well as the proton and hydrogen affinities of the corresponding  $\mathbf{1}^-$  are also defined as the enthalpy changes of **1** to gain a neutral hydrogen atom in acetonitrile and the enthalpy changes of  $\mathbf{1}^-$  to gain a proton and to gain a neutral hydrogen atom in acetonitrile, which can be used to measure hydrogen-obtaining abilities of **1** and to measure proton-obtaining abilities and hydrogen-obtaining abilities of  $\mathbf{1}^-$ , respectively.

In order to obtain the hydrogen affinity of **1** and the proton affinity and the hydrogen affinity of the corresponding radical carbanion of **1** ( $\mathbf{1}^-$ ), three thermodynamic cycles were constructed according to the chemical process of **1** to obtain a hydride anion in acetonitrile (Scheme 2). From the three thermodynamic cycles, the eqs 5–7<sup>20</sup> were formed according to Hess' law, respectively. In eqs 5–7,  $\Delta H_{\text{H-A}}(\mathbf{1})$  and  $\Delta H_{\text{HA}}(\mathbf{1})$  are the enthalpy changes of **1** to obtain a hydride anion in acetonitrile and to obtain a neutral hydrogen atom in acetonitrile, respectively; the  $\Delta H_{\text{HA}}(\mathbf{1}^-)$  and  $\Delta H_{\text{PA}}(\mathbf{1}^-)$  are the enthalpy changes of  $\mathbf{1}^-$  to obtain a neutral hydrogen atom in acetonitrile and to obtain a proton in acetonitrile, respectively;  $E^\circ_{\text{ox}}(\mathbf{1H}^-)$ ,  $E^\circ_{\text{red}}(\mathbf{1})$ ,  $E^\circ(\text{H}^{0-})$ , and  $E^\circ(\text{H}^{+0})$  are the standard redox potentials

(20) It should be pointed out herein that we used the term free energy change  $\Delta G_{\text{et}}$  to replace the enthalpy change  $\Delta H_{\text{et}}$  in eqs 5–7 for the electron transfer processes. The validation of this treatment is that entropies associated with electron transfer are negligible, which has been verified by the previous papers: (a) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 344. (b) Li, X.; Zhu, X.-Q.; Zhang, F.; Wang, X.-X.; Cheng, J.-P. *J. Org. Chem.* **2008**, *130*, 2501.

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SCHEME 1. Possible Pathways of the Reduction of **1** by Hydride AnionSCHEME 2. Three Thermodynamic Cycles Constructed on the Basis of the Reaction of Dienes (**1**) with Hydride Anion ( $\text{H}^-$ )

of  $\mathbf{1H}^-$ ,  $\mathbf{1}$ ,  $\mathbf{H}^+$ , and  $\mathbf{H}^-$  in acetonitrile, respectively. Evidently, it is not difficult to obtain the enthalpy changes of  $\mathbf{1}$  to obtain a neutral hydrogen atom in acetonitrile and the enthalpy changes of  $\mathbf{1}^-$  to obtain a neutral hydrogen atom and to obtain a proton in acetonitrile, if only  $\Delta H_{\text{H-A}}(\mathbf{1})$ ,  $E^\circ_{\text{ox}}(\mathbf{1H}^-)$ ,  $E^\circ_{\text{red}}(\mathbf{X})$ ,  $E^\circ(\text{H}^{0/-})$ , and  $E^\circ(\text{H}^{+/0})$  are available. In fact,  $\Delta H_{\text{H-A}}(\mathbf{1})$  can be available from the above work (Table 1), the standard redox potentials of  $E^\circ(\text{H}^{0/-})$  and  $E^\circ(\text{H}^{+/0})$  can be obtained from literature,<sup>21</sup>  $E^\circ_{\text{ox}}(\mathbf{1H}^-)$ ,  $E^\circ_{\text{red}}(\mathbf{1})$  can be measured by using CV and OSWV methods (Figures 2 and 3).<sup>22</sup> The detailed values of  $\Delta H_{\text{H-A}}(\mathbf{1})$ ,  $\Delta H_{\text{HA}}(\mathbf{1}^-)$  and  $\Delta H_{\text{PA}}(\mathbf{1}^-)$  in acetonitrile are listed in Table 2, the standard redox potentials of  $\mathbf{1}$  and  $\mathbf{1H}^-$  are summarized in Table 1.

$$\Delta H_{\text{HA}}(\mathbf{1}) = \Delta H_{\text{H-A}}(\mathbf{1}) - F[E^\circ(\text{H}^{0/-}) - E^\circ(\mathbf{1H}^{0/-})] \quad (5)$$

$$\Delta H_{\text{PA}}(\mathbf{1}^-) = \Delta H_{\text{H-A}}(\mathbf{1}) - F[E^\circ(\text{H}^{+/0}) - E^\circ(\mathbf{1}^{0/-})] \quad (6)$$

$$\Delta H_{\text{HA}}(\mathbf{1}^-) = \Delta H_{\text{PA}}(\mathbf{1}^-) - F[E^\circ(\mathbf{1H}^{0/-}) - E^\circ(\text{H}^{+/0})] \quad (7)$$

Table 2 shows that the hydride affinities of the dienes ( $\mathbf{1}$ ) in acetonitrile range from  $-71.6$  to  $-73.9$  kcal mol $^{-1}$  for the cumulated dienes ( $\mathbf{1a}$ ), from  $-48.2$  to  $-49.7$  kcal mol $^{-1}$  for the isolated dienes ( $\mathbf{1b}$ ), and from  $-45.0$  to  $-46.5$  kcal mol $^{-1}$  for the conjugated dienes ( $\mathbf{1c}$ ). By simply comparing  $\mathbf{1a}$ ,  $\mathbf{1b}$ , and  $\mathbf{1c}$  with the same substituent (such as  $\text{G} = \text{H}$ ), it is found that the hydride affinity of the cumulated diene ( $-73.1$  kcal mol $^{-1}$ ) is greater than that of the corresponding isolated diene ( $-49.1$  kcal mol $^{-1}$ ) by  $-24.0$  kcal mol $^{-1}$  and greater than that of the corresponding conjugated diene ( $-45.9$  kcal mol $^{-1}$ ) by  $-27.2$  kcal mol $^{-1}$ , which indicates that the hydride-obtaining ability of the cumulated diene is not only much larger than that of the corresponding conjugated diene but also much larger than that of the corresponding isolated diene. In fact, many experimental observations have shown that cumulated diene is a good hydride acceptor, one of the two conterminous double bonds

can be easily reduced by reducing agents or broken by nucleophilic agents.<sup>2</sup> In order to examine the origins of the greater hydride affinity of the cumulated diene, the relative energies of the three dienes ( $\mathbf{1a}$ ,  $\mathbf{1b}$ , and  $\mathbf{1c}$ ) and their reduced products ( $\mathbf{1aH}^-$ ,  $\mathbf{1bH}^-$ , and  $\mathbf{1cH}^-$ ) were estimated according to their hydrogenation heats<sup>23</sup> and the hydride affinities; the results are shown in Figure 4, where the hydrogenation heat of the isolated diene  $\mathbf{1b}$  ( $\text{G} = \text{H}$ ) was regarded as the reference. From Figure 4, it is found there are two factors that give rise to the greater hydride affinity of cumulated diene compared with that of the corresponding isolated one. One is that the ground-state energy of the cumulated diene is higher than that of the isolated diene due to repulsive interaction between the con-

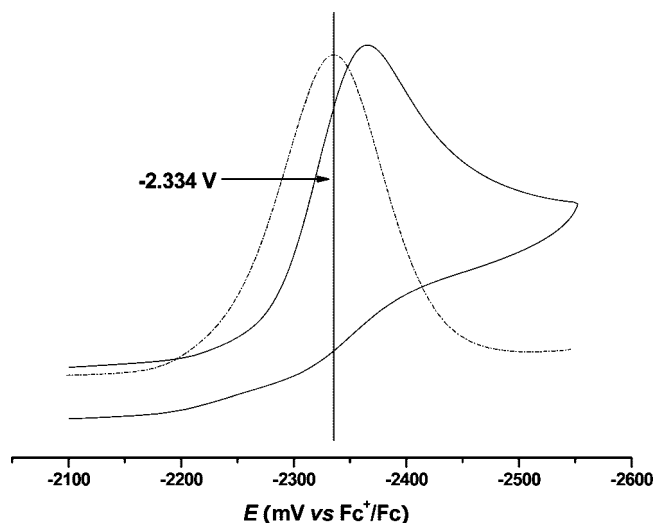
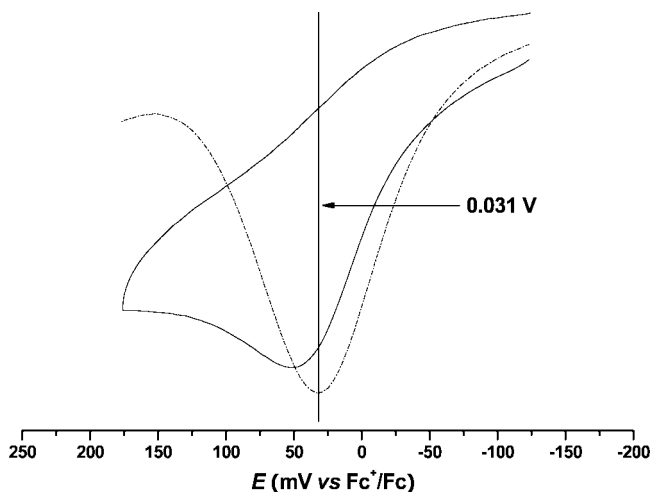
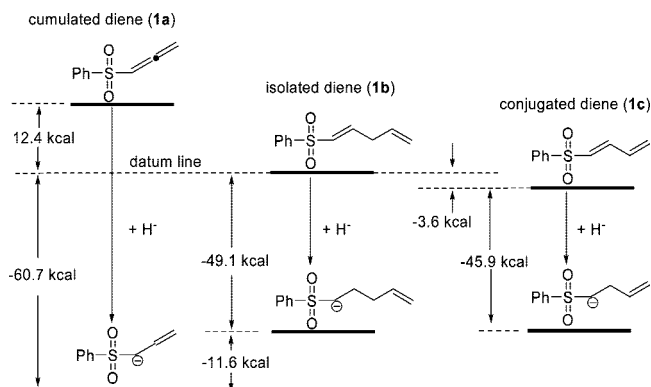


FIGURE 2. Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) of  $\mathbf{1a}$  ( $\text{G} = \text{CH}_3$ ) in deaerated acetonitrile containing  $0.1$  M  $n\text{-Bu}_4\text{NPF}_6$  as supporting electrolyte: (full line) CV graph, sweep rate =  $0.1$  V/s, (dashed line) OSWV graph.



**FIGURE 3.** Cyclic voltammery (CV) and Osteryoung square wave voltammery (OSWV) of  $1aH^-$  ( $G = CH_3$ ) in deaerated acetonitrile containing 0.1 M  $n-Bu_4NPF_6$  as supporting electrolyte: (full line) CV graph, sweep rate = 0.1 V/s, (dashed line) OSWV graph.



**FIGURE 4.** Relative energies of the three dienes (**1a**, **1b**, and **1c**) together with their corresponding reduced products ( $1aH^-$ ,  $1bH^-$ , and  $1cH^-$ ) compared with the isolated diene (**1b**), where the relative energies of the three dienes were estimated from the hydrogenation heats of their corresponding analogues.<sup>23</sup>

minus two  $\pi$ -electrons in **1a**; the other is that the ground-state energy of the reduced product of the cumulated diene ( $1aH^-$ ) is lower than that of the reduced product of the isolated diene ( $1bH^-$ ) owing to the delocalization of the negative charge in  $1aH^-$ . Sum of the two effects makes the hydride affinity of the cumulated diene become much greater than that of the corresponding isolated one (**1b**) by 24.0 kcal mol<sup>-1</sup>. From the relative ground-state energies of  $1aH^-$  and  $1bH^-$ , an interesting estimation about the delocalization energy of the negative charge over the adjacent  $\pi$ -orbital in  $1aH^-$  can be derived (-11.6 kcal mol<sup>-1</sup>) for the first time.

However, if the hydride affinities of the cumulated dienes are compared with the hydride affinities of some well-known primary benzyl carboniums in acetonitrile solution, it is found that the hydride affinities of the cumulated dienes (-71.6 to -73.9 kcal mol<sup>-1</sup>) are smaller than those of the corresponding primary benzylic carbonium ions in acetonitrile solution (e.g., -106, -112, -118, and -121 kcal mol<sup>-1</sup> for 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub><sup>+</sup>, 4-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub><sup>+</sup>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub><sup>+</sup>, and 4-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub><sup>+</sup>, respectively) by 30–40 kcal mol<sup>-1</sup>.<sup>24</sup> Examining the reaction (eq

1) shows that unlike the reduction of benzylic carbonium ions by hydride, the reduction of the cumulated dienes by hydride involves not only the formation of a new C–H  $\sigma$ -bond to release energy but also the dissociation of one C=C  $\pi$ -bond to consume energy. Hence, the magnitude of hydride affinities for the cumulated dienes should be equal to the heterolytic dissociation energy of the newly formed C–H  $\sigma$ -bond minus the heterolytic dissociation energy of the broken old C=C  $\pi$ -bond. Thus, it is not difficult to understand why the hydride affinity scale of the cumulated dienes is much smaller than that of the primary benzylic carbonium ions, since the hydride affinities of the primary benzylic carbonium ions do not involve the heterolytic dissociation energy of the broken C=C  $\pi$ -bond.

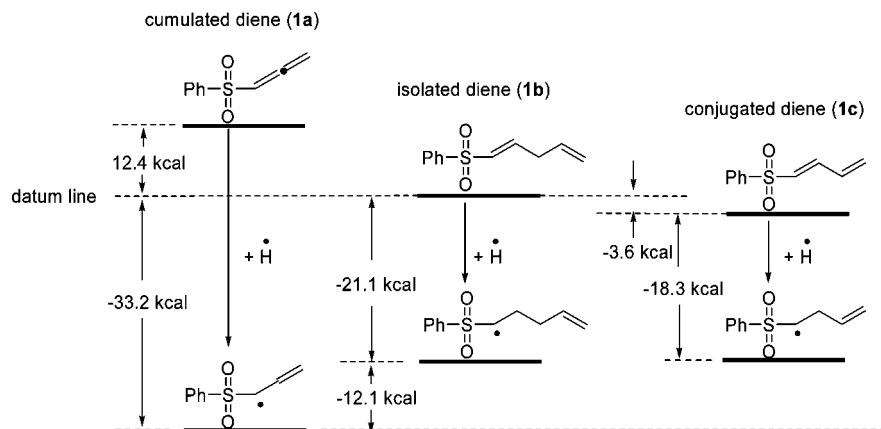
When the hydride affinities of the isolated dienes **1b** and the conjugated dienes **1c** were compared, it was found that the hydride affinities of the isolated dienes are greater than those of the corresponding conjugated ones by 3.1–3.2 kcal mol<sup>-1</sup>. Since these differences in hydride affinities (3.1–3.2 kcal mol<sup>-1</sup>) all are close to the resonance energy of the conjugated dienes **1c** (~3.6 kcal mol<sup>-1</sup>),<sup>23</sup> it is believed that the relative thermodynamic stability of the two carbanions  $1bH^-$  and  $1cH^-$  should be close to each other. In fact, from the structures of  $1bH^-$  and  $1cH^-$ , a reasonable explanation can be easily derived that unlike in  $1aH^-$ , the negative charge center and the terminal  $\pi$ -orbital in  $1bH^-$  and  $1cH^-$  are intervened by two or three single bonds, which of course does not result in a large difference between  $1bH^-$  and  $1cH^-$  in stability due to the effect of the terminal  $\pi$ -orbital on the delocalization of the negative charge center.

In Table 2, the hydrogen affinities of dienes **1** in acetonitrile range from -45.3 to -44.6 kcal mol<sup>-1</sup> for **1a**, from -21.4 to -20.4 kcal mol<sup>-1</sup> for **1b**, and from -18.5 to 17.3 kcal mol<sup>-1</sup> for **1c**. Since the hydrogen affinities of **1a** are greater than those of **1b** by 23.9–24.5 kcal mol<sup>-1</sup> and greater than those of **1c** by 26.9–27.3 kcal mol<sup>-1</sup>, the hydrogen-obtaining abilities of the cumulated dienes should be not only larger than those of the corresponding isolated dienes but also larger than those of the corresponding conjugated dienes. By examining the ground-state energies of the three dienes (**1**) and their corresponding neutral radicals ( $1H^\bullet$ ) using the similar method described above (see Figure 5), it is found that the ground-state energy of  $1aH^\bullet$  is much lower than that of  $1bH^\bullet$ , and the energy difference of the two neutral radicals (12.1 kcal mol<sup>-1</sup>) is close to the energy difference of the two corresponding parent dienes (12.4 kcal mol<sup>-1</sup>), which indicates that the conjugation of a single p-electron with the conterminous  $\pi$ -orbital in  $1aH^\bullet$  (12.1 kcal mol<sup>-1</sup> for the resonance energy) is also one main origin of the greater hydrogen affinity of cumulated diene compared with that of the isolated one. Since the energy difference of the two neutral radicals mainly results from the resonance interaction of the negative charge with the terminal  $\pi$ -orbital in  $1aH^\bullet$ , the resonance energy of p- $\pi$  in  $1aH^\bullet$  can be estimated from the relative ground-state energies of  $1aH^\bullet$  and  $1bH^\bullet$ ; the result is -12.1 kcal mol<sup>-1</sup>. This value (-12.1 kcal mol<sup>-1</sup>) is close to or slightly larger than the C–H bond dissociation energy difference between CH<sub>2</sub>=CHCH<sub>2</sub>-H (allylic) (88.9 kcal mol<sup>-1</sup>)<sup>25</sup> and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-H (100.9 kcal mol<sup>-1</sup>),<sup>25</sup> which means that the hydrogen affinities of the dienes determined in this work should be reasonable and reliable, and the same should hold true for

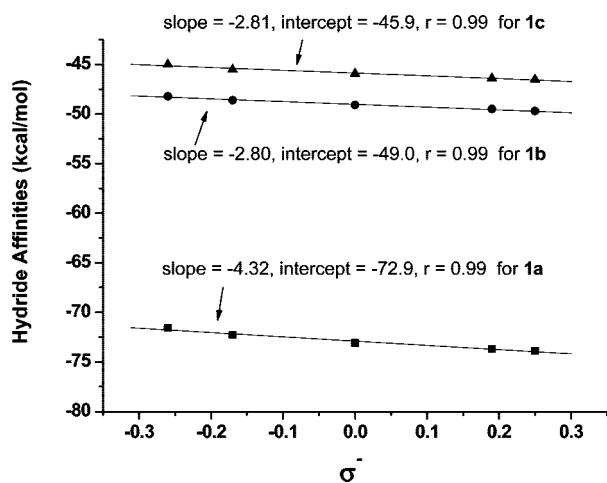
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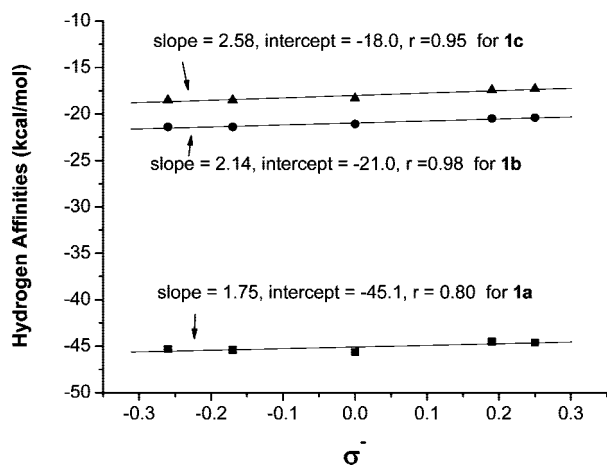
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**FIGURE 5.** Relative energies of the three dienes (**1a**, **1b**, and **1c**) together with their corresponding neutral radicals (**1aH•**, **1bH•**, and **1cH•**) compared with the isolated diene (**1b**), where the relative energies of the three dienes were estimated from the hydrogenation heats of their corresponding analogues.<sup>23</sup>



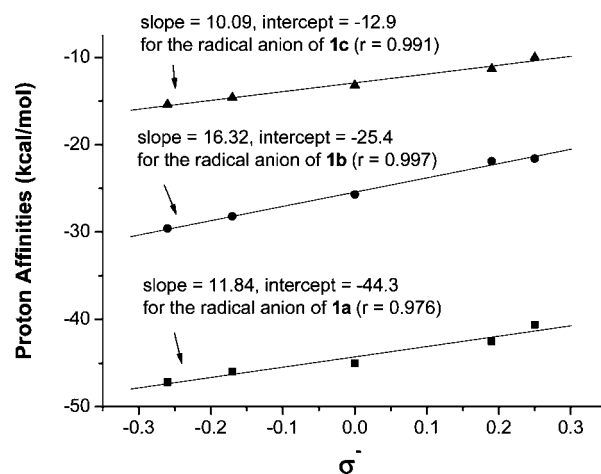
**FIGURE 6.** Plots of  $\Delta H_{H-A}(1)$  against the Brown substituent parameters  $\sigma^-$ .



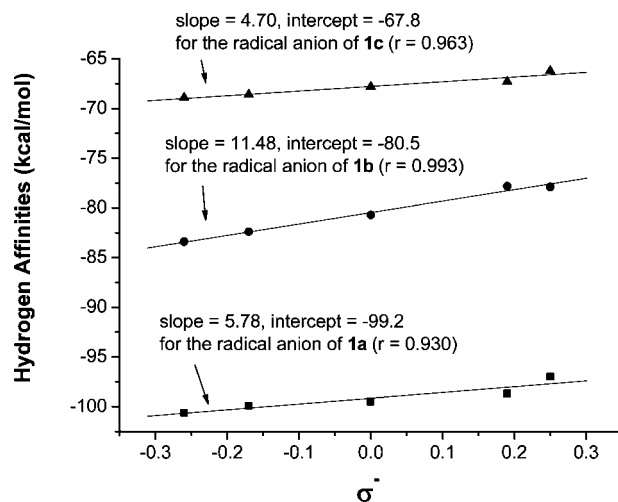
**FIGURE 7.** Plots of  $\Delta H_{HA}(1)$  against the Brown substituent parameters  $\sigma^-$ .

their hydride affinities in acetonitrile. The hydrogen affinities of dienes **1** are smaller than the corresponding hydride affinities by about 26.3–29.3 kcal mol<sup>-1</sup>, that is, dienes **1** should prefer hydride to the neutral hydrogen atom.

Proton affinities of the dienes radical anions (**1**<sup>-•</sup>) in acetonitrile (Table 2) range from -40.6 to -47.2 kcal mol<sup>-1</sup>, from -21.6 to -29.6 kcal mol<sup>-1</sup>, and from -10.0 to -15.4 kcal



**FIGURE 8.** Plots of  $\Delta H_{PA}(1^{-\bullet})$  against the Brown substituent parameters  $\sigma^-$ .



**FIGURE 9.** Plots of  $\Delta H_{HA}(1^{-\bullet})$  against the Brown substituent parameters  $\sigma^-$ .

mol<sup>-1</sup> for **1a**<sup>-•</sup>, **1b**<sup>-•</sup>, and **1c**<sup>-•</sup>, respectively. Since the proton affinities of **1a**<sup>-•</sup> are quite negative (more negative than -40 kcal mol<sup>-1</sup>), the radical anions should belong to strong bases, but the corresponding neutral radical **1aH•** should be a weak acid. As to **1b**<sup>-•</sup> and **1c**<sup>-•</sup>, since their proton affinities all are not quite negative (more positive than -30 kcal mol<sup>-1</sup>), **1b**<sup>-•</sup>

and  $\mathbf{1c}^{\bullet-}$  should be mild or weak bases, the corresponding neutral radical  $\mathbf{1bH}^{\bullet}$  and  $\mathbf{1cH}^{\bullet}$  should mild or strong acids. From Table 2, we also find that the hydrogen affinities of the radical anions ( $\mathbf{1}^{\bullet-}$ ) of dienes in acetonitrile range from  $-97.0$  to  $-100.6$  kcal mol $^{-1}$ , from  $-77.9$  to  $-83.4$  kcal mol $^{-1}$ , and from  $-66.2$  to  $-68.9$  kcal mol $^{-1}$  for  $\mathbf{1a}^{\bullet-}$ ,  $\mathbf{1b}^{\bullet-}$ , and  $\mathbf{1c}^{\bullet-}$ , respectively. Since the hydrogen affinities of  $\mathbf{1a}^{\bullet-}$  are greater than the corresponding hydrogen affinities of  $\mathbf{1b}^{\bullet-}$  by 20 kcal mol $^{-1}$  and greater than the corresponding hydrogen affinities of  $\mathbf{1c}^{\bullet-}$  by 30 kcal mol $^{-1}$ , the hydrogen-obtaining abilities of  $\mathbf{1a}^{\bullet-}$  are much larger than those of  $\mathbf{1b}^{\bullet-}$  and  $\mathbf{1c}^{\bullet-}$ . If the hydrogen affinities of  $\mathbf{1a}^{\bullet-}$  are compared with their proton affinities, it is found that the hydrogen affinities of  $\mathbf{1a}^{\bullet-}$  are greater than their corresponding proton affinities by more than 50 kcal mol $^{-1}$ , and thus the large gap of energy indicates that the hydrogen-obtaining potency of  $\mathbf{1a}^{\bullet-}$  is much larger than their proton-obtaining potency. Conceivably, if reduction of the cumulated dienes by a hydride donor were initiated by single-electron transfer, hydrogen atom transfer in the second step to the formed  $\mathbf{1a}^{\bullet-}$  should be much easier than proton transfer to the same radical anions, and the hydrogen atom transfer rate is possibly diffusion-controlled.

The effect of the remote substituent G on the hydride and hydrogen affinities of the dienes as well as on the proton and hydrogen affinities of the radical anions of dienes in acetonitrile was examined according to some typical substituent parameters:  $\sigma$ ,  $\sigma^+$ ,  $\sigma^o$ ,  $\sigma^*$  and  $\sigma^-$ , respectively. The results show that only  $\sigma^-$  has a linear relationship with  $\Delta H_{H-A}(\mathbf{1})$ ,  $\Delta H_{HA}(\mathbf{1})$ ,  $\Delta H_{PA}(\mathbf{1}^{\bullet-})$ , and  $\Delta H_{HA}(\mathbf{1}^{\bullet-})$  (see Figures 6–9), which indicates that the Brown linear free energy relationship holds in all of the 12 chemical processes. Since the slopes of the lines are negative for  $\Delta H_{H-A}(\mathbf{1})$  but positive for  $\Delta H_{HA}(\mathbf{1})$ ,  $\Delta H_{PA}(\mathbf{1}^{\bullet-})$ , and  $\Delta H_{HA}(\mathbf{1}^{\bullet-})$ , it is evident that an electron-withdrawing group can increase the hydride-obtaining potency of  $\mathbf{1}$  but decrease the hydrogen-obtaining potency of  $\mathbf{1}$  and  $\mathbf{1}^{\bullet-}$  and decrease the proton-obtaining potency of  $\mathbf{1}^{\bullet-}$ .

From the slopes and intercepts of the 12 straight lines, the 12 mathematical formulas (eqs 8–19) can be derived, respectively. Evidently, for any substituent at the *para* position of dienes  $\mathbf{1}$  and the corresponding radical anions,  $\mathbf{1}^{\bullet-}$ , it is not difficult to safely estimate the values of the corresponding  $\Delta H_{H-A}(\mathbf{1})$ ,  $\Delta H_{HA}(\mathbf{1})$ ,  $\Delta H_{PA}(\mathbf{1}^{\bullet-})$  and  $\Delta H_{HA}(\mathbf{1}^{\bullet-})$  according to eqs 8–19, as long as the corresponding Brown substituent parameters ( $\sigma^-$ ) are available and the standard deviation of the estimations is less than  $\pm 0.25$  kcal mol $^{-1}$ . It is evident that the 12 formulas should have a very extensive application in the predication of the related thermodynamic potencies of the dienes and their reaction intermediates to capture hydride, hydrogen atom, or proton in acetonitrile.

$$\Delta H_{H-A}(\mathbf{1}) = -4.32\sigma^- - 72.9 \text{ for } \mathbf{1a} \quad (8)$$

$$\Delta H_{H-A}(\mathbf{1}) = -2.80\sigma^- - 49.0 \text{ for } \mathbf{1b} \quad (9)$$

$$\Delta H_{H-A}(\mathbf{1}) = -2.81\sigma^- - 45.9 \text{ for } \mathbf{1c} \quad (10)$$

$$\Delta H_{HA}(\mathbf{1}) = 1.75\sigma^- - 45.1 \text{ for } \mathbf{1a} \quad (11)$$

$$\Delta H_{HA}(\mathbf{1}) = 2.14\sigma^- - 21.0 \text{ for } \mathbf{1b} \quad (12)$$

$$\Delta H_{HA}(\mathbf{1}) = 2.58\sigma^- - 18.0 \text{ for } \mathbf{1c} \quad (13)$$

$$\Delta H_{PA}(\mathbf{1}^{\bullet-}) = 11.84\sigma^- - 44.3 \text{ for } \mathbf{1a}^{\bullet-} \quad (14)$$

$$\Delta H_{PA}(\mathbf{1}^{\bullet-}) = 16.32\sigma^- - 25.4 \text{ for } \mathbf{1b}^{\bullet-} \quad (15)$$

$$\Delta H_{PA}(\mathbf{1}^{\bullet-}) = 10.09\sigma^- - 12.9 \text{ for } \mathbf{1c}^{\bullet-} \quad (16)$$

$$\Delta H_{HA}(\mathbf{1}^{\bullet-}) = 5.78\sigma^- - 99.2 \text{ for } \mathbf{1a}^{\bullet-} \quad (17)$$

$$\Delta H_{HA}(\mathbf{1}^{\bullet-}) = 11.48\sigma^- - 80.5 \text{ for } \mathbf{1b}^{\bullet-} \quad (18)$$

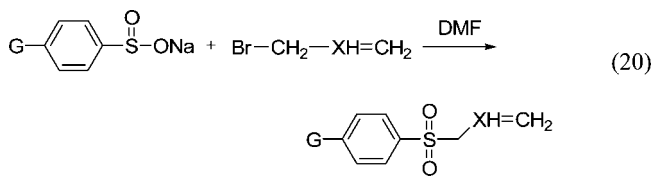
$$\Delta H_{HA}(\mathbf{1}^{\bullet-}) = 4.70\sigma^- - 67.8 \text{ for } \mathbf{1c}^{\bullet-} \quad (19)$$

## Conclusions

In this work, the hydride affinities of 15 polarized cumulated, isolated, and conjugated dienes  $\mathbf{1}$  in acetonitrile were determined by experimental method, while the hydrogen affinities of  $\mathbf{1}$  and the proton affinities and hydrogen affinities of  $\mathbf{1}^{\bullet-}$  were estimated using thermodynamic cycles according to Hess' law. After analyses of the experimental results and detailed examination of the effect of the remote substituents on the hydride affinities, hydrogen affinities, and the proton affinities, the following conclusions can be made: (i) The hydride-obtaining ability of the cumulated dienes is not only much larger than that of the corresponding conjugated dienes but also larger than that of the corresponding isolated ones. In general, cumulated dienes should belong to strong hydride acceptors, but the corresponding isolated and conjugated dienes should be weak hydride acceptors. (ii) The hydrogen-obtaining ability of cumulated dienes is much larger than that of the corresponding isolated and conjugated dienes, but they are all weak hydrogen atom acceptors. (iii) The proton-obtaining ability of the radical anions of the cumulated dienes is much larger than that of the corresponding isolated and conjugated dienes. Among the three types of the radical anions, the radical anions of the cumulated dienes should belong to strong *brønst* base, the radical anions of the isolated dienes should belong to the middle-strong *brønst* base, but the radical anions of the conjugated dienes should belong to weak *brønst* base. (iv) The hydrogen-obtaining abilities of the radical anions of the cumulated, isolated, and conjugated dienes all are quite large, larger than those of the corresponding neutral dienes. Especially, for the radical anions of the cumulated dienes, the hydrogen affinities are larger than or close to  $-100$  kcal/mol, which means that if reduction of the cumulated dienes were initiated by single-electron transfer, the following hydrogen atom transfer should be extremely fast and possibly diffusion-controlled, which means that in most cases the reduction of cumulated dienes generally take place by hydride transfer in one step. (v) The substituent effects hold excellent Brown linear free energy relationships on the hydride, hydrogen, and proton affinities of the three types of dienes and their radical anions, which means that for any remote substitution of the dienes and their radical anions, the hydride, hydrogen, and proton affinities can be safely estimated according to the relative linear relationships as long as the corresponding Brown substituent parameters ( $\sigma^-$ ) are available. It is clear that these thermodynamic data could be not only very valuable when choosing suitable reducing agents for dienes reductions and carrying out detailed thermodynamic analysis on the mechanism but also helpful in understanding the especially high chemical activities of the cumulated dienes relative to the corresponding isolated or conjugated one. To our best knowledge, this paper is the first report about hydride affinities of allenes in solution.

## Experimental Section

**Materials.** All reagents were of commercial quality from freshly opened containers or were purified before use. Reagent grade acetonitrile was refluxed over  $\text{KMnO}_4$  and  $\text{K}_2\text{CO}_3$  for several hours and was doubly distilled over  $\text{P}_2\text{O}_5$  under argon before use. The commercial tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ , Aldrich) was recrystallized from  $\text{CH}_2\text{Cl}_2$  and was vacuum-dried at 110 °C overnight before preparation of supporting electrolyte solution. 9-Phenylxanthylum ( $\text{PhXn}^+\text{ClO}_4^-$ ) was synthesized according to literature methods.<sup>26</sup> Compounds  $\mathbf{1H}_2$  were obtained from the reaction of sodium *para*-substituted phenyl sulfinate with the corresponding bromides in anhydrous DMF. The yields are generally more than 90%. The products were identified by comparison with the authentic values according to their  $^1\text{H}$  NMR.<sup>27</sup> The carbanions of  $\mathbf{1H}_2$  ( $\mathbf{1H}^-$ ) were prepared according to Arnett's method.<sup>28</sup> The anion precursor ( $\mathbf{1H}_2$ ) was dissolved in dry acetonitrile, and then a slightly excess amount of  $\text{KH}$  was added. The mixture was stirred at room temperature for about 20 min and then filtered directly into the reaction vessel. All operations were carried out in an argon-filled glovebox. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the formed anions were in agreement with the reported in the previous work.<sup>29</sup>



(X = C, CHCH, CHCH<sub>2</sub>CH)

**Product Analysis.**  $\mathbf{1H}^-$  ( $\text{K}^+$  as counterion) was treated by  $\text{PhXn}^+\text{ClO}_4^-$  in dry  $\text{CH}_3\text{CN}$  to give the corresponding dienes by

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hydride transfer; the product was identified by comparison with the authentic  $^1\text{H}$  NMR data, e.g.,  $\delta$  7.94(d, 2H), 7.58(m, 3H), 6.25(d, 1H), 5.44(d, 2H) for  $\mathbf{1a}$  (G = H).

**Measurement of Redox Potentials.** The electrochemical experiments were carried out by cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) using a BAS-100B electrochemical apparatus in deaerated acetonitrile under argon atmosphere at 298 K as described previously.<sup>30</sup> *n*- $\text{Bu}_4\text{NPF}_6$  (0.1 M) in acetonitrile was employed as the supporting electrolyte. A standard three-electrode cell consists of a glassy carbon disk as work electrode, a platinum wire as a counter electrode, and 0.1 M  $\text{AgNO}_3/\text{Ag}$  (in 0.1 M *n*- $\text{Bu}_4\text{NPF}_6$  in acetonitrile) as reference electrode. The ferrocenium/ferrocene redox couple ( $\text{Fc}^+/\text{Fc}$ ) was taken as the internal standard. The reproducibilities of the potentials were usually  $\leq 5$  mV for ionic species and  $\leq 10$  mV for neutral species.

**Isothermal Titration Calorimetry (ITC).** The titration experiments were performed on a CSC4200 isothermal titration calorimeter in acetonitrile at 298 K as described previously.<sup>31</sup> The performance of the calorimeter was checked by measuring the standard heat of neutralization of an aqueous solution of sodium hydroxide with a standard aqueous HCl solution. Data points were collected every 2 s. The heat of reaction was determined following 10 automatic injections from a 250  $\mu\text{L}$  injection syringe containing a standard solution ( $\sim 3$  mM) into the reaction cell (1.30 mL) containing 1 mL other concentrated reactant ( $\sim 10$  mM). Injection volume (8  $\mu\text{L}$ ) were delivered in a 0.5 s time interval with 400 s between every two injections. The reaction heat was obtained by integration of each peak except the first. Note: typically the first injection shows less heat than expected. This is often due to diffusion across the tip of the needle or to difficulties in positioning the buret drive.

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