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Determination of Thermodynamic Affinities of Various Polar Olefins as Hydride, Hydrogen Atom, and Electron Acceptors in Acetonitrile

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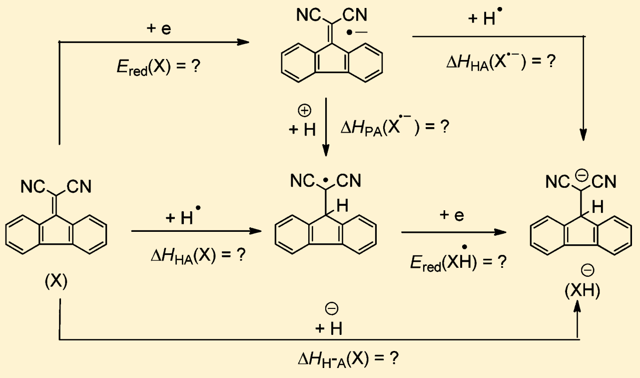
Supporting Information

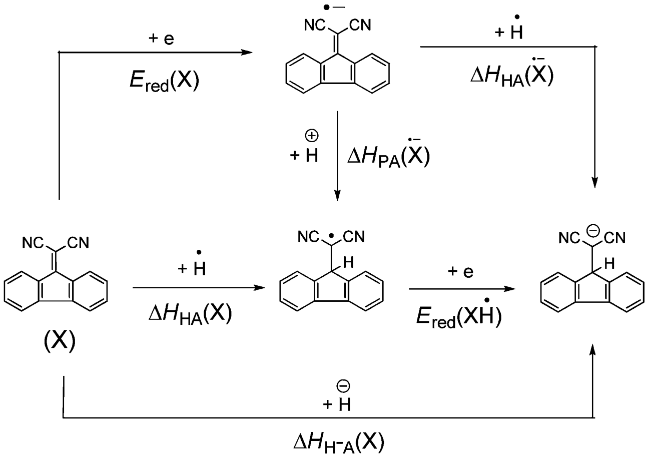
ABSTRACT: A series of 69 polar olefins with various typical structures (**X**) were synthesized and the thermodynamic affinities (defined in terms of the molar enthalpy changes or the standard redox potentials in this work) of the polar olefins obtaining hydride anions, hydrogen atoms, and electrons, the thermodynamic affinities of the radical anions of the polar olefins ($\mathbf{X}^{\bullet-}$) obtaining protons and hydrogen atoms, and the thermodynamic affinities of the hydrogen adducts of the polar olefins ($\mathbf{XH}^{\bullet}$) obtaining electrons in acetonitrile were determined using titration calorimetry and electrochemical methods. The pure C═C π-bond heterolytic and homolytic dissociation energies of the polar olefins (**X**) in acetonitrile and the pure C═C π-bond homolytic dissociation energies of the radical anions of the polar olefins ($\mathbf{X}^{\bullet-}$) in acetonitrile were estimated. The remote substituent effects on the six thermodynamic affinities of the polar olefins and their related reaction intermediates were examined using the Hammett linear free-energy relationships; the results show that the Hammett linear free-energy relationships all hold in the six chemical and electrochemical processes. The information disclosed in this work could not only supply a gap of the chemical thermodynamics of olefins as one class of very important organic unsaturated compounds but also strongly promote the fast development of the chemistry and applications of olefins.



INTRODUCTION

Olefin is one type of very important organic unsaturated compounds,[1] especially the polar olefins.[2−9] The reduction of the polar olefin is one of the most fundamental organic chemical reactions, which is extensively applied in organic synthesis[10] and the chemical industry.[11] Because olefins can be reduced by hydride donors, such as NADH, $NaBH_4$, and $LiAiH_4$, neutral hydrogen atom donors, such as H_2, SnH_4, and $(CH_3)_3SiH$, and electron donors, such as SmI_2, Fc, TMPA, Na, K, etc.,[12,13] there is no doubt that the hydride affinity, hydrogen atom affinity, and electron affinity of various polar olefins in solution are very important thermodynamic parameters to scale the reduction ability of olefins in solution. In addition, since the reduction of olefins can involve the formation of various intermediates of olefins, such as radical anions, neutral radicals, and carbanions (Scheme 1), it is clear that the proton and hydrogen atom affinities of olefin radical anions as well as the electron affinity of the neutral radical in solution are also important thermodynamic parameters, which can be directly used to quantitatively scale the characteristic chemical properties of the related reaction intermediates. In this work, we synthesize 69 typical polar olefins (**X**) (**X** = **1**−**21** in Scheme 2) and determine their hydride affinity in acetonitrile by using experimental methods. Meanwhile, the hydrogen atom affinity and electron affinity of 69 typical polar olefins in acetonitrile, the proton and hydrogen atom affinities of the olefin radical anions, and the electron affinity of the neutral radicals in acetonitrile were also estimated in terms of the thermodynamic cyclic theory and related electrochemical parameters.[14]

Scheme 1. Possible Reduction Mechanism of Olefin 11 by Addition of Hydride Anion



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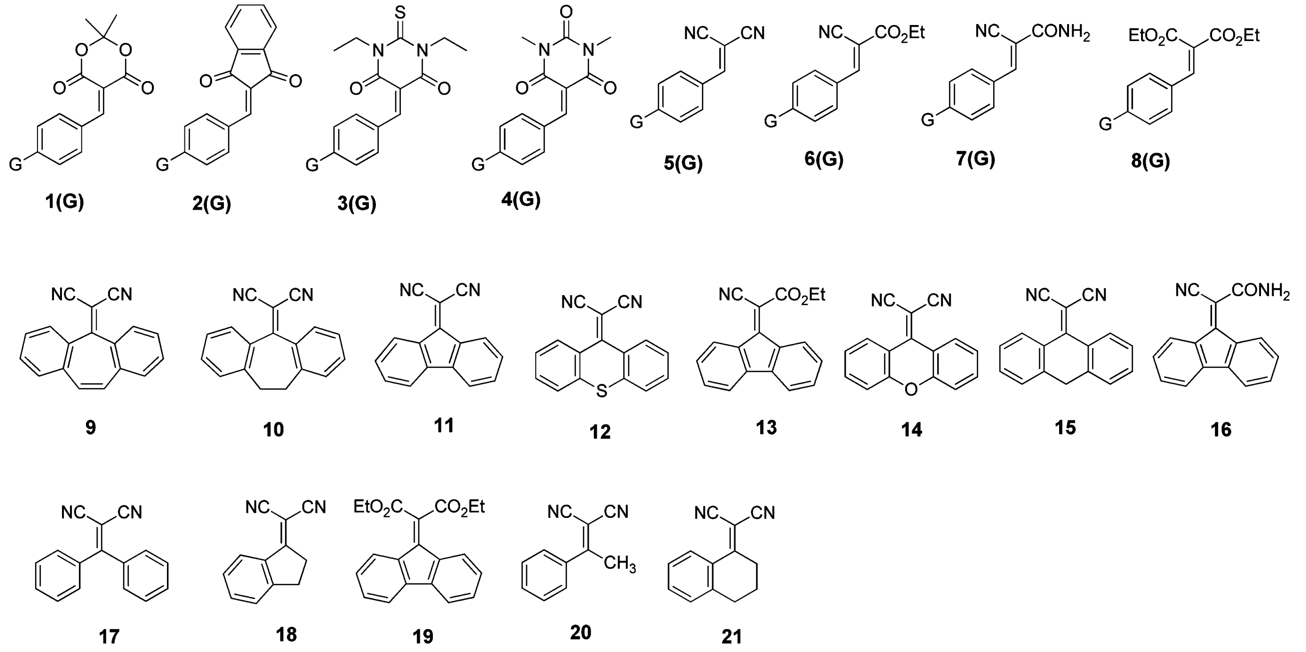
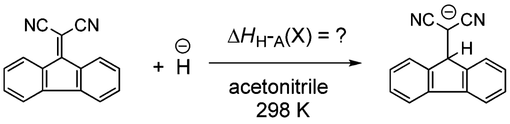
Scheme 2. Structures and Numbers of the Polar Olefins X (1−21) [G = CH_3O (a), CH_3 (b), H (c), Cl (d), Br (e), CF_3 (f), and NO_2 (g)] Examined in This Work



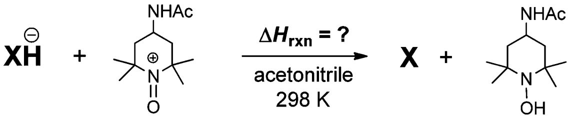
■ RESULTS

The hydride affinity of the olefins (**X**) in this work is defined as the reaction molar enthalpy change of olefins **X** with hydride ions in acetonitrile to form the corresponding carbanions ($\mathbf{XH}^-$) (eqs 1 and 2) at 298 K, $\Delta H_{\mathrm{H^-A}}(\mathbf{X})$, which can be used



(1)

to directly scale the hydride-obtaining ability of olefins. Because the free hydride ion in acetonitrile is not available, it is clear that it is difficult to directly determine the hydride affinity of the polar olefins in acetonitrile by using conventional experimental methods. However, the hydride affinity of **X** in solution, $\Delta H_{\mathrm{H^-A}}(\mathbf{X})$, can be obtained from the reaction enthalpy change of the corresponding carbanions $\mathbf{XH}^-$ with a strong hydride acceptor, such as 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium (Ac-tempo$^+$) (eqs 3 and 4). In eq 4, ΔH_{rxn} is



(3)

the molar enthalpy change of the reaction (eq 3) in acetonitrile, which can be determined by using titration calorimetry (Figure 1); $\Delta H_{\mathrm{H^-A}}(\text{Ac-tempo}^+)$ is the hydride affinity of Ac-tempo$^+$ in acetonitrile, which has been determined previously (−105.6 kcal/mol).[15] The molar enthalpy changes of the reactions of $\mathbf{XH}^-$ with Ac-tempo$^+$ (eq 3) are listed in Table 1. The detailed hydride affinities of the 69 polar olefins **X** in acetonitrile are summarized in Table 2.

$$\Delta H_{\mathrm{H^-A}}(\mathrm{X}) = H_{\mathrm{f}}(\mathrm{XH^-}) - [H_{\mathrm{f}}(\mathrm{X}) + H_{\mathrm{f}}(\mathrm{H^-})] \qquad (2)$$

$$\Delta H_{\mathrm{H^-A}}(\mathrm{X}) = \Delta H_{\mathrm{H^-A}}(\text{Ac-tempo}^+) - \Delta H_{\mathrm{rxn}} \qquad (4)$$

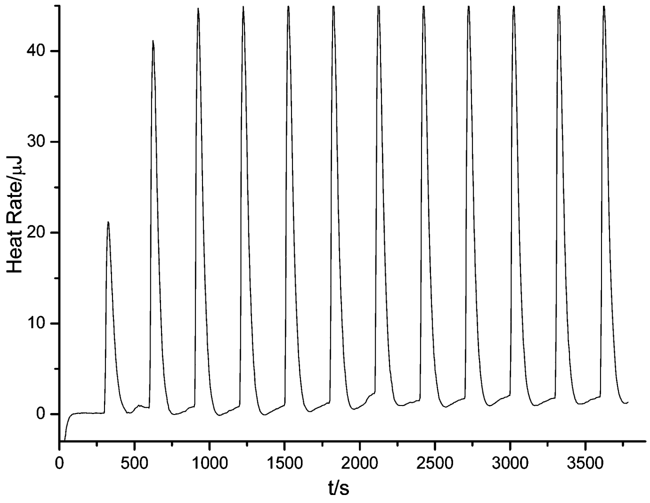


Figure 1. Isothermal titration calorimetry (ITC) for the reaction heat of carbanion $\mathbf{11H}^-$ with Ac-tempo$^+ClO_4^-$ in acetonitrile at 298 K. Titration was conducted by adding 10 μL of Ac-tempo$^+ClO_4^-$ (2.0 mM) every 400 s into the acetonitrile containing the $\mathbf{11H}^-$ (ca. 10.0 mM), which was obtained in situ from the reaction of the corresponding saturated neutral compounds of olefin $\mathbf{11H_2}$ with KH.

The hydrogen affinities of olefins (**X**) as well as the hydrogen affinities and proton affinities of the olefin radical anions ($\mathbf{X}^{\bullet-}$) in this work are also defined as the molar enthalpy changes of the corresponding chemical processes. To obtain the molar enthalpy change values of the olefins to gain a hydrogen atom, as well as the molar enthalpy change values of $\mathbf{X}^{\bullet-}$ to gain a hydrogen atom and proton in acetonitrile, three thermodynamic cycles were constructed according to the reduction process of **X** by hydride anions to form the corresponding hydride addition of olefins ($\mathbf{XH}^-$) in acetonitrile (Scheme 3). From the three thermodynamic cycles, three eqs 5−7[16] can be derived according to Hess's law. In eqs 5−7, $\Delta H_{\mathrm{H^-A}}(\mathbf{X})$, and $\Delta H_{\mathrm{HA}}(\mathbf{X})$ are the hydride affinities and hydrogen affinities of **X**

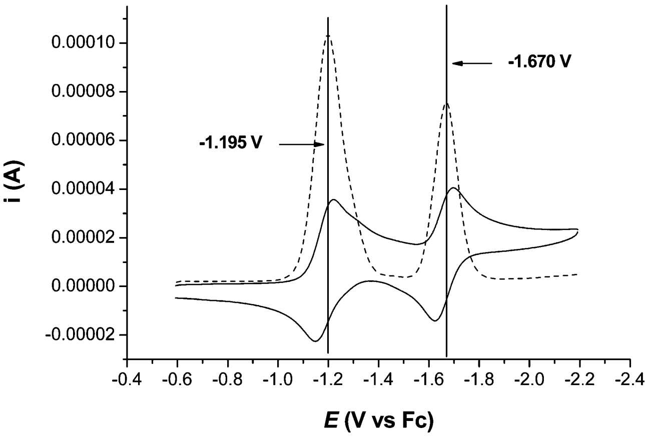


Figure 2. Cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (OSWV) of olefin **13** in deaerated acetonitrile containing 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte. Solid line: CV graph (sweep rate = 0.1 V/s). Dashed line: OSWV graph.

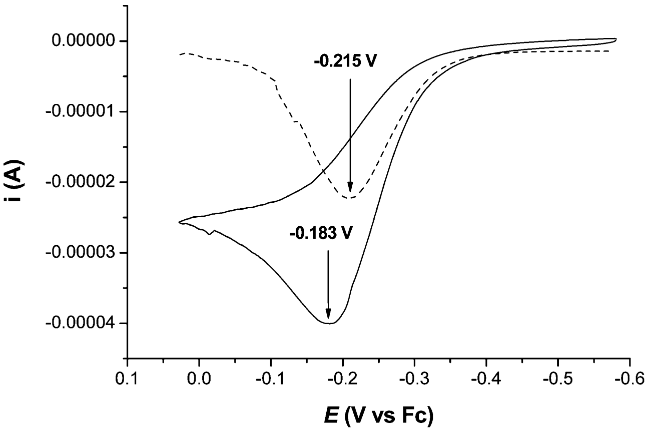
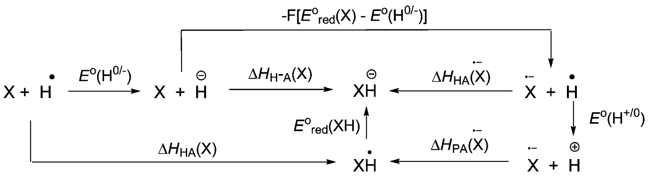


Figure 3. Cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (OSWV) of anion **11H**$^-$ in deaerated acetonitrile containing 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte. Solid line: CV graph (sweep rate = 0.1 V/s). Dashed line: OSWV graph.

Scheme 3. Three Thermodynamic Cycles Were Constructed on the Basis of the Reduction of Olefins (X) by Hydride Ion (H^-)



in acetonitrile, respectively; $\Delta H_{HA}(\mathbf{X}^{\bullet-})$ and $\Delta H_{PA}(\mathbf{X}^{\bullet-})$ are the hydrogen affinities and proton affinities of $\mathbf{X}^{\bullet-}$ in acetonitrile, respectively; $E^{\circ}_{red}(\mathbf{X})$, $E^{\circ}_{red}(\mathbf{XH}^{\bullet})$, $E^{\circ}(H^{0/-})$, and $E^{\circ}(H^{+/0})$ are the standard redox potentials of **X**, $\mathbf{XH}^{\bullet}$, H^+, and H^- in acetonitrile, respectively. It is obvious that $\Delta H_{HA}(\mathbf{X})$, $\Delta H_{HA}(\mathbf{X}^{\bullet-})$, and $\Delta H_{PA}(\mathbf{X}^{\bullet-})$ can be obtained as long as the $\Delta H_{H^-A}(\mathbf{X})$, $E^{\circ}_{red}(\mathbf{X})$, $E^{\circ}_{red}(\mathbf{XH}^{\bullet})$, $E^{\circ}(H^{0/-})$, and $E^{\circ}(H^{+/0})$ are available. In fact, $\Delta H_{H^-A}(\mathbf{X})$ are available from the above work in Table 2, $E^{\circ}(H^{0/-})$ and $E^{\circ}(H^{+/0})$ can be achieved from the literature,[17] and $E^{\circ}_{red}(\mathbf{X})$ and $E^{\circ}_{red}(\mathbf{XH}^{\bullet})$ can be obtained from direct experimental measurements (see Figures 2 and 3). The detailed values of $\Delta H_{H^-A}(\mathbf{X})$, $\Delta H_{HA}(\mathbf{X})$, $\Delta H_{HA}(\mathbf{X}^{\bullet-})$, and $\Delta H_{PA}(\mathbf{X}^{\bullet-})$ together with the reduction potentials of the 69 **X** and $\mathbf{XH}^{\bullet}$ in acetonitrile are all summarized in Table 2.

$$\Delta H_{HA}(X) = \Delta H_{H^-A}(X) - F[E^{\circ}(H^{0/-}) - E^{\circ}_{red}(XH^{\bullet})] \tag{5}$$

$$\Delta H_{HA}(X^{\bullet-}) = \Delta H_{H^-A}(X) - F[E^{\circ}(H^{0/-}) - E^{\circ}_{red}(X)] \tag{6}$$

$$\Delta H_{PA}(X^{\bullet-}) = \Delta H_{HA}(X^{\bullet-}) - F[E^{\circ}(H^{+/0}) - E^{\circ}_{red}(XH^{\bullet})] \tag{7}$$

■ DISCUSSION

Hydride Affinity Scale of the Polar Olefins in Acetonitrile. The second column in Table 2 shows that the hydride affinities of the 69 polar olefins (**1**−**21**) in acetonitrile range from −52.8 kcal/mol for **8**(**a**) to −68.0 kcal/mol for **1**(**g**). Because the hydride affinities of the 69 polar olefins in acetonitrile are all quite small, all the 69 polar olefins generally are not strong hydride acceptors. By simply comparing the hydride affinities of the polar olefins (**1**−**21**) with the same substituent (e.g., G = H in Figure 4), it is found that the hydride affinities of the 21 typical polar olefins decrease in the following order: **1** (−65.9 kcal/mol) > **2** (−65.0 kcal/mol) > **3** (−64.0 kcal/mol) > **9** (−63.9 kcal/mol) > **10** (−63.1 kcal/mol) > **4**, **11** (−62.8 kcal/mol) > **12** (−62.6 kcal/mol) > **13** (−61.5 kcal/mol) > **5c** (−61.0 kcal/mol) > **14** (−60.8 kcal/mol) > **15** (−60.0 kcal/mol) > **6** (−59.0 kcal/mol) > **16** (−58.4 kcal/mol) > **17** (−58.0 kcal/mol) > **18** (−56.9 kcal/mol) > **19** (−56.5 kcal/mol) > **20** (−55.8 kcal/mol) > **7c** (−55.7 kcal/mol) > **21** (−55.6 kcal/mol) > **8c** (−53.7 kcal/mol).[18] If the hydride affinities of the 21 typical olefins in acetonitrile are compared with the enthalpy change values of some well-known organic and inorganic hydride donors to release hydride anions in acetonitrile solution, it is found that most of the polar olefins cannot be directly reduced by mild organic hydride donors, for example, 1-benzyl-1,4-dihydronicotinamide (64.2 kcal/mol)[19] and 9,10-dihydroacridine (81.1 kcal/mol),[19] but can be reduced by stronger organic hydride donors, such as 1-benzyl-1,4-dihydropyridine (53.0 kcal/mol)[19] and 1-benzyl-3-methyl-1,4-dihydropyridine (48.0 kcal/mol),[19] or by inorganic hydride donors, such as $NaBH_3CN$ or $NaBH_4$.

If the hydride affinities of the 69 polar olefins (**1**−**21**) are compared with those of some primary benzyl carbonium ions in acetonitrile (e.g., −106, −112, −118, and −121 kcal/mol for 4-$CH_3OC_6H_4CH_2^+$, 4-$MeC_6H_4CH_2^+$, $C_6H_5CH_2^+$, and 4-ClC_6H_4-CH_2^+, respectively),[20] it is found that the hydride affinities of the 69 polar olefins (**1**−**21**) are much smaller than those of the corresponding primary benzyl carboniums ions. From eq 1, it is clear that, unlike the reduction of benzyl carbonium ions by hydride ion, the reduction of the olefins by hydride ion not only involves the formation of one new C−H bond to release energy but also involves dissociation of one old C=C *π* bond to consume energy; that is, the magnitude of hydride affinities of the olefins should be equal to the heterolytic dissociation energy of the newly formed C−H *σ* bond minus the heterolytic dissociation energy of the broken C=C *π* bond. Thus, it is not difficult to understand why the hydride affinities of olefins in acetonitrile are much smaller than those of the corresponding primary benzyl carbonium ions in acetonitrille; the reason is that the reduction of the primary benzyl carbonium ions by hydride anion does not involve the heterolytic dissociation of any *π* bond.

Table 1. Molar Reaction Enthalpies of eq 3 in Acetonitrile at 298 K (kcal/mol) and Redox Potentials of X and XH$^-$ in Acetonitrile (V vs Fc$^{+/0}$)

		E_{red}(**X**)[b]		E_{ox}(**XH**$^-$)[b]	
olefins (**X**)	ΔH_{rxn}[a]	CV	OSWV	CV	OSWV
1(**a**–**g**)					
p-CH$_3$O (**a**)	−40.6	−1.644	−1.617	−0.248	−0.276
p-CH$_3$ (**b**)	−40.3	−1.602	−1.572	−0.243	−0.272
p-H (**c**)	−39.7	−1.522	−1.494	−0.228	−0.257
p-Cl (**d**)	−39.2	−1.435	−1.407	−0.210	−0.240
p-Br (**e**)	−39.1	−1.434	−1.407	−0.210	−0.240
p-CF$_3$ (**f**)	−38.4	−1.290	−1.261	−0.186	−0.215
p-NO$_2$ (**g**)	−37.6	−1.183	−1.157	−0.168	−0.199
2(**a**–**g**)					
p-CH$_3$O (**a**)	−41.6	−1.435	−1.411	−0.212	−0.242
p-CH$_3$ (**b**)	−41.3	−1.395	−1.370	−0.207	−0.236
p-H (**c**)	−40.6	−1.300	−1.276	−0.194	−0.223
p-Cl (**d**)	−40.1	−1.211	−1.184	−0.177	−0.205
p-Br (**e**)	−40.1	−1.215	−1.191	−0.177	−0.205
p-CF$_3$ (**f**)	−39.3	−1.065	−1.040	−0.152	−0.181
p-NO$_2$ (**g**)	−38.7	−0.970	−0.942	−0.136	−0.166
3(**a**–**g**)					
p-CH$_3$O (**a**)	−42.7	−1.625	−1.600	−0.241	−0.269
p-CH$_3$ (**b**)	−42.3	−1.572	−1.544	−0.234	−0.263
p-H (**c**)	−41.6	−1.486	−1.461	−0.220	−0.248
p-Cl (**d**)	−41.1	−1.352	−1.325	0.199	0.229
p-Br (**e**)	−41.0	−1.354	−1.326	−0.200	−0.228
p-CF$_3$ (**f**)	−40.4	−1.205	−1.178	−0.173	−0.203
p-NO$_2$ (**g**)	−39.9	−1.083	−1.057	−0.153	−0.184
4(**a**–**g**)					
p-CH$_3$O (**a**)	−43.4	−1.510	−1.481	−0.230	−0.261
p-CH$_3$ (**b**)	−43.2	−1.472	−1.444	−0.224	−0.254
p-H (**c**)	−42.8	−1.411	−1.382	−0.209	−0.240
p-Cl (**d**)	−42.0	−1.327	−1.298	−0.191	−0.220
p-Br (**e**)	−42.0	−1.322	−1.295	−0.190	−0.220
p-CF$_3$ (**f**)	−41.5	−1.222	−1.196	−0.164	−0.193
p-NO$_2$ (**g**)	−41.0	−1.125	−1.098	−0.147	−0.175
5(**a**–**g**)					
p-CH$_3$O (**a**)	−45.2	−1.556	−1.533	−0.236	−0.264
p-CH$_3$ (**b**)	−45.0	−1.501	−1.480	−0.234	−0.261
p-H (**c**)	−44.6	−1.444	−1.424	−0.213	−0.240
p-Cl (**d**)	−44.0	−1.337	−1.315	−0.186	−0.216
p-Br (**e**)	−44.1	−1.328	−1.304	−0.185	−0.216
p-CF$_3$ (**f**)	−43.0	−1.155	−1.135	−0.167	−0.197
p-NO$_2$ (**g**)	−42.6	−1.028	−1.003	−0.142	−0.171
6(**a**–**g**)					
p-CH$_3$O (**a**)	−47.5	−1.721	−1.700	−0.262	−0.290
p-CH$_3$ (**b**)	−47.2	−1.676	−1.651	−0.255	−0.284
p-H (**c**)	−46.6	−1.597	−1.573	−0.240	−0.271
p-Cl (**d**)	−46.2	−1.501	−1.480	−0.221	−0.250
p-Br (**e**)	−46.1	−1.499	−1.474	−0.221	−0.250
p-CF$_3$ (**f**)	−45.3	−1.332	−1.308	−0.195	−0.225
p-NO$_2$ (**g**)	−41.8	−1.186	−1.161	−0.177	−0.206
7(**a**–**g**)					
p-CH$_3$O (**a**)	−50.5	−1.944	−1.922	−0.293	−0.323
p-CH$_3$ (**b**)	−50.3	−1.884	−1.860	−0.286	−0.315
p-H (**c**)	−49.9	−1.793	−1.771	−0.273	−0.301
p-Cl (**d**)	−49.0	−1.666	−1.642	−0.253	−0.282
p-Br (**e**)	−48.9	−1.666	−1.642	−0.252	−0.282
p-CF$_3$ (**f**)	−48.4	−1.504	−1.481	−0.224	−0.253
p-NO$_2$ (**g**)	−47.9	−1.377	−1.354	−0.204	−0.234
8(**a**–**g**)					
p-CH$_3$O (**a**)	−52.8	−2.074	−2.047	−0.321	−0.350
p-CH$_3$ (**b**)	−52.5	−2.033	−2.004	−0.313	−0.341
p-H (**c**)	−51.9	−1.953	−1.924	−0.298	−0.330
p-Cl (**d**)	−51.4	−1.858	−1.830	−0.280	−0.311
p-Br (**e**)	−51.3	−1.860	−1.831	−0.280	−0.310
p-CF$_3$ (**f**)	−50.6	−1.711	−1.681	−0.254	−0.282
p-NO$_2$ (**g**)	−49.9	−1.603	−1.574	−0.233	−0.259
9	−41.7	−1.275	−1.268	−0.142	−0.169
10	−42.5	−1.223	−1.210	−0.131	−0.157
11	−42.8	−1.100	−1.085	−0.183	−0.215
12	−43.0	−1.379	−1.388	−0.248	−0.272
13	−44.1	−1.200	−1.185	−0.209	−0.235-
14	−44.8	−1.295	−1.290	−0.197	−0.227
15	−45.6	−1.325	−1.324	−0.221	−0.252
16	−47.2	−1.372	−1.357	−0.235	−0.270
17	−47.6	−1.484	−1.464	−0.103	−0.134
18	−48.7	−1.675	−1.652	−0.290	−0.322
19	−49.1	−1.453	−1.436	−0.257	−0.288
20	−49.8	−1.667	−1.636	−0.284	−0.312
21	−50.0	−1.616	−1.612	−0.261	−0.292

[a] ΔH_{rxn} obtained from the reaction heats of eq 3 by switching the sign and measured by titration calorimetry in acetonitrile at 298 K. The data given in kcal/mol were average values of at least three independent runs. The reproducibility is ±0.5 kcal/mol. [b] Measured by CV and OSWV methods in acetonitrile at 298 K; the unit is in volts vs Fc$^{+/0}$ and reproducible to 5 mV or better.

To estimate the C═C π-bond heterolytic dissociation energies of the polar olefins in acetonitrile, the hydride affinities of some benzyl cations in acetonitrile can be regarded as the approximations of the releasing energy due to the new C–H σ-bond formation after the C═C π-bond heterolytic dissociation when the olefins **1**–**21** were reduced by hydride anion; the reason is that the structure of the benzyl cation is the kindred efficient structure of olefins when the C═C π bond was broken by heterolytic dissociation.[21] Thus, the C═C π-bond heterolytic dissociation enthalpies of olefins **1**–**21** in acetonitrile can be estimated according to the difference in the hydride affinities of the polar olefins and the corresponding benzyl cations. The detailed C═C π-bond heterolytic dissociation enthalpies of olefins **1**–**21** in acetonitrile are listed in Table 3. By using the similar method, the homolytic C═C π-bond dissociation enthalpies of **1**–**21** and (C═C)$^{\bullet-}$ π-bond dissociation enthalpies of **1**$^{\bullet-}$ to **21**$^{\bullet-}$ can also be estimated;[22] the detailed results are also listed in Table 3. From Table 3, it is clear that the heterolytic C═C π-bond dissociation enthalpies of olefins **1**–**21** range from 42.0 kcal/mol for **1**(**a**) to 73.3 kcal/mol for **8**(**g**). The homolytic C═C π-bond dissociation enthalpies of olefins **1**–**21** range from 41.7 kcal/mol for **1**(**g**) to 53.4 kcal/mol for **8**(**a**). Because the heterolytic C═C π-bond dissociation enthalpies of the polar olefins (**1**–**21**) are large (generally larger than 50 kcal/mol), it is not difficult to understand why the hydride affinities of the olefins are smaller than those of the primary benzyl carboniums ions. However, if the hydride affinities and the heterolytic C═C π-bond dissociation enthalpies of olefins **5a** and **5g** are examined together (see Figure 5), a surprising result can be found that, for the olefins, the larger the heterolytic C═C π-bond dissociation energy of the olefins, the larger the hydride affinity of the olefins. The

Table 2. Hydride and Hydrogen Affinities of Olefins (X), Hydrogen and Proton Affinities of $X^{\bullet -}$ as Well as the Reduction Potentials of X and $XH^{\bullet}$ (V vs $Fc^{+/0}$), and Activation Coefficients of the C=C π Bond by Electron Addition (A_e%) in Acetonitrile

X	$\Delta H_{H^-A}(X)^a$	$\Delta H_{HA}(X)^b$	$\Delta H_{HA}(X^{\bullet -})^b$	$\Delta H_{PA}(X^{\bullet -})^b$	$E^o_{red}(X)^c$	$E^o_{red}(XH^{\bullet})^c$	$A_e\%^d$
1(a−g)							
p-CH_3O (a)	−65.0	−45.1	−76.1	−29.2	−1.617	−0.276	40.71
p-CH_3 (b)	−65.3	−45.3	−75.3	−28.3	−1.572	−0.272	39.85
p-H (c)	−65.9	−45.6	−74.1	−26.8	−1.494	−0.257	38.54
p-Cl (d)	−66.4	−45.7	−72.6	−24.9	−1.407	−0.240	37.11
p-Br (e)	−66.5	−45.8	−72.7	−25.0	−1.407	−0.240	37.06
p-CF_3 (f)	−67.2	−45.9	−70.1	−21.7	−1.261	−0.215	34.49
p-NO_2 (g)	−68.0	−46.3	−68.5	−19.8	−1.157	−0.199	32.32
2(a−g)							
p-CH_3O (a)	−64.0	−43.3	−70.3	−22.6	−1.411	−0.242	38.40
p-CH_3 (b)	−64.3	−43.5	−69.7	−21.8	−1.370	−0.236	37.59
p-H (c)	−65.0	−43.9	−68.2	−20.1	−1.276	−0.223	35.66
p-Cl (d)	−65.5	−44.0	−66.6	−18.0	−1.184	−0.205	33.96
p-Br (e)	−65.5	−44.0	−66.7	−18.2	−1.191	−0.205	34.12
p-CF_3 (f)	−66.3	−44.2	−64.1	−14.9	−1.040	−0.181	30.98
p-NO_2 (g)	−66.9	−44.5	−62.4	−12.9	−0.942	−0.166	28.73
3(a−g)							
p-CH_3O (a)	−62.9	−42.8	−73.6	−26.5	−1.600	−0.269	41.78
p-CH_3 (b)	−63.3	−43.1	−72.7	−25.5	−1.544	−0.263	40.70
p-H (c)	−64.0	−43.5	−71.5	−23.9	−1.461	−0.248	39.20
p-Cl (d)	−64.5	−43.5	−68.8	−20.8	−1.325	0.229	36.78
p-Br (e)	−64.6	−43.6	−69.0	−20.9	−1.326	−0.228	36.78
p-CF_3 (f)	−65.2	−43.6	−66.1	−17.5	−1.178	−0.203	34.05
p-NO_2 (g)	−65.7	−43.7	−63.9	−14.8	−1.057	−0.184	31.58
4(a−g)							
p-CH_3O (a)	−62.2	−42.0	−70.1	−22.9	−1.481	−0.261	40.18
p-CH_3 (b)	−62.4	−42.0	−69.5	−22.1	−1.444	−0.254	39.56
p-H (c)	−62.8	−42.1	−68.5	−20.7	−1.382	−0.240	38.53
p-Cl (d)	−63.6	−42.4	−67.3	−19.1	−1.298	−0.220	36.99
p-Br (e)	−63.6	−42.4	−67.2	−19.0	−1.295	−0.220	36.93
p-CF_3 (f)	−64.1	−42.3	−65.5	−16.6	−1.196	−0.193	35.39
p-NO_2 (g)	−64.6	−42.4	−63.7	−14.4	−1.098	−0.175	33.47
5(a−g)							
p-CH_3O (a)	−60.4	−40.2	−69.5	−22.4	−1.533	−0.264	42.15
p-CH_3 (b)	−60.6	−40.4	−68.5	−21.3	−1.480	−0.261	41.09
p-H (c)	−61.0	−40.3	−67.6	−19.9	−1.424	−0.240	40.44
p-Cl (d)	−61.6	−40.3	−65.7	−17.4	−1.315	−0.216	38.63
p-Br (e)	−61.5	−40.2	−65.4	−17.1	−1.304	−0.216	38.45
p-CF_3 (f)	−62.6	−40.9	−62.6	−13.8	−1.135	−0.197	34.64
p-NO_2 (g)	−63.0	−40.7	−59.9	−10.6	−1.003	−0.171	32.08
6(a−g)							
p-CH_3O (a)	−58.1	−38.5	−71.1	−24.5	−1.700	−0.290	45.81
p-CH_3 (b)	−58.4	−38.7	−70.3	−23.5	−1.651	−0.284	44.94
p-H (c)	−59.0	−39.0	−69.1	−22.0	−1.573	−0.271	43.54
p-Cl (d)	−59.4	−38.9	−67.3	−19.8	−1.480	−0.250	42.20
p-Br (e)	−59.5	−39.0	−67.3	−19.8	−1.474	−0.250	42.02
p-CF_3 (f)	−60.3	−39.2	−64.3	−16.2	−1.308	−0.225	38.94
p-NO_2 (g)	−60.8	−39.3	−61.4	−12.8	−1.161	−0.206	35.96
7(a−g)							
p-CH_3O (a)	−55.1	−36.3	−73.2	−27.4	−1.922	−0.323	50.44
p-CH_3 (b)	−55.3	−36.3	−72.0	−26.0	−1.860	−0.315	49.57
p-H (c)	−55.7	−36.4	−70.3	−24.0	−1.771	−0.301	48.27
p-Cl (d)	−56.6	−36.8	−68.3	−21.5	−1.642	−0.282	46.02
p-Br (e)	−56.7	−36.9	−68.4	−21.6	−1.642	−0.282	45.95
p-CF_3 (f)	−57.2	−36.8	−65.1	−17.7	−1.481	−0.253	43.54
p-NO_2 (g)	−57.7	−36.8	−62.7	−14.8	−1.354	−0.234	41.25
8(a−g)							
p-CH_3O (a)	−52.8	−34.6	−73.8	−28.6	−2.047	−0.350	53.10
p-CH_3 (b)	−53.1	−34.7	−73.1	−27.7	−2.004	−0.341	52.53

Table 2. continued

X	$\Delta H_{H^-A}(\mathbf{X})^a$	$\Delta H_{HA}(\mathbf{X})^b$	$\Delta H_{HA}(\mathbf{X}^{\bullet-})^b$	$\Delta H_{PA}(\mathbf{X}^{\bullet-})^b$	$E^o_{red}(\mathbf{X})^c$	$E^o_{red}(\mathbf{XH}^\bullet)^c$	$A_e\%^d$
p-H (**c**)	−53.7	−35.1	−71.9	−26.2	−1.924	−0.330	51.23
p-Cl (**d**)	−54.2	−35.2	−70.2	−24.1	−1.830	−0.311	49.98
p-Br (**e**)	−54.3	−35.2	−70.3	−24.2	−1.831	−0.310	49.96
p-CF_3 (**f**)	−55.0	−35.2	−67.6	−20.8	−1.681	−0.282	47.83
p-NO_2 (**g**)	−55.7	−35.4	−65.8	−18.5	−1.574	−0.259	46.17
9	−63.9	−41.5	−66.9	−17.5	−1.268	−0.169	37.93
10	−63.1	−40.5	−64.8	−15.1	−1.210	−0.157	37.55
11	−62.8	−41.5	−61.6	−13.3	−1.085	−0.215	32.63
12	−62.6	−42.6	−68.4	−21.4	−1.388	−0.272	37.69
13	−61.5	−40.7	−62.6	−14.7	−1.185	−0.235	35.05
14	−60.8	−39.8	−64.3	−16.3	−1.290	−0.227	38.17
15	−60.0	−39.6	−64.3	−16.8	−1.324	−0.252	38.50
16	−58.4	−38.4	−63.5	−16.4	−1.357	−0.270	39.55
17	−58.0	−34.8	−65.6	−15.4	−1.464	−0.134	46.87
18	−56.9	−38.1	−68.8	−22.9	−1.652	−0.322	44.66
19	−56.5	−36.9	−63.4	−16.8	−1.436	−0.288	41.82
20	−55.8	−36.7	−67.3	−21.2	−1.636	−0.312	45.43
21	−55.6	−36.1	−66.6	−20.0	−1.612	−0.292	45.80

[a] $\Delta H_{H^-A}(\mathbf{X})$ values of olefins **1−21** were estimated from eq 4, taking $\Delta H_{H^-A}(\text{Ac-tempo}^+)$ = −105.6 kcal/mol. [b] $\Delta H_{HA}(\mathbf{X})$, $\Delta H_{HA}(\mathbf{X}^{\bullet-})$, and $\Delta H_{PA}(\mathbf{X}^{\bullet-})$ were estimated from eqs 5−7, respectively, taking $E^o(H^{+/0})$ = −2.307 (V vs $Fc^{+/0}$) and $E^o(H^{0/-})$ = −1.137 V (V vs $Fc^{+/0}$) (Fc = ferrocene), and choosing the reduction potentials of **X** and **XH**$^\bullet$ measured by the OSWV method (Table 1) as $E^o_{red}(\mathbf{X})$ and $E^o_{red}(\mathbf{XH}^\bullet)$, since the values from OSWV were identified to be closer to the corresponding standard redox potentials than the values from CV. [c] The values derived by OSWV were chosen as the standard reduction potentials of **X** and **XH**$^\bullet$. [d] Derived from eq 8.

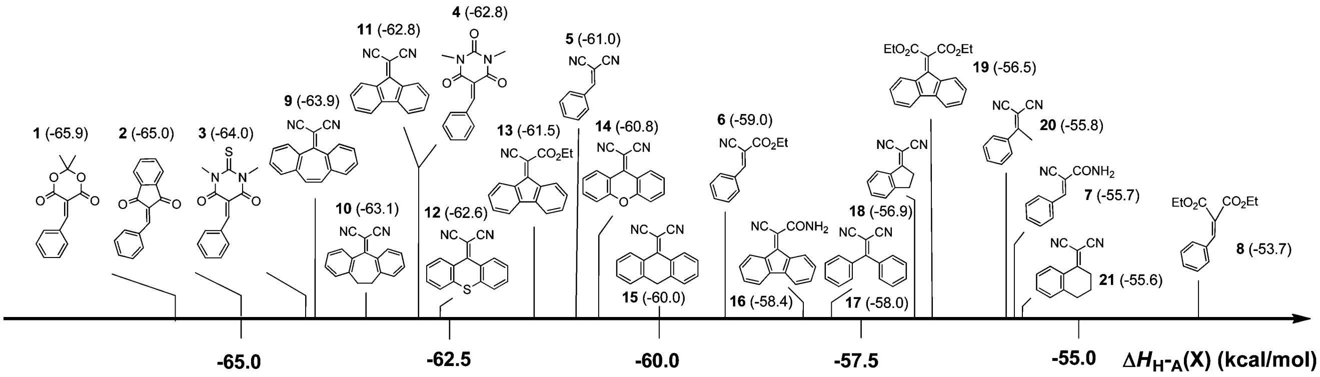


Figure 4. Scale of molar enthalpy change for the 21 typical polar olefins to capture hydride anions in acetonitrile.

reason could be that the large C═C π-bond heterolytic dissociation energy can result in the larger releasing energy to form the new C−H σ bond.

From Table 3, if the heterolytic C═C π-bond dissociation energies and the corresponding homolytic C═C π-bond dissociation energies are compared, it is found that the heterolytic C═C π-bond dissociation enthalpy of the olefins especially with electron-withdrawing groups, such as CF_3 and NO_2, are generally quite greater than the corresponding homolytic C═C π-bond dissociation enthalpy, which indicates that, in the addition reaction of the C═C double bond of olefins, the radical mechanism should be preferable to the ionic mechanism. For the olefins carrying strong electron-donating groups, such as CH_3O, the ionic mechanism has also competitive potential.

Hydrogen Affinity Scale of the Polar Olefins in Acetonitrile. The third column in Table 2 shows that the hydrogen affinity scale of the 69 polar olefins (**1−21**) in acetonitrile ranges from −34.6 kcal/mol for **8**(**a**) to −46.3 kcal/mol for **1**(**g**). If the hydrogen affinities of the 69 polar olefins **X** are compared, it is found that, when the substituent is the same (e.g., G = H), the power of the olefins to obtain a hydrogen atom is decreased in the following order: **1** (−45.6 kcal/mol) > **2** (−43.9 kcal/mol) > **3** (−43.5 kcal/mol) > **12** (−42.6 kcal/mol) > **4c** (−42.1 kcal/mol) > **11**, **9** (−41.5 kcal/mol) > **13** (−40.7 kcal/mol) > **10** (−40.5 kcal/mol) > **5** (−40.3 kcal/mol) > **14** (−39.8 kcal/mol) > **15** (−39.6 kcal/mol) > **6c** (−39.0 kcal/mol) > **16** (−38.4 kcal/mol) > **18** (−38.1 kcal/mol) > **19** (−36.9 kcal/mol) > **20** (−36.7 kcal/mol) > **7c** (−36.4 kcal/mol) > **21** (−36.1 kcal/mol) > **8c** (−53.1 kcal/mol) > **17** (−34.8 kcal/mol) (see Figure 6). Because the hydrogen affinities of the most polar olefins (**1−21**) are all quite small negative values less negative than −50 kcal/mol, the polar olefins, in general, are all not good hydrogen atom acceptors, which means that, when the olefins were reduced by the common hydrogen donors, such as SnH_4, Me_3SiH, and H_2, the reactions should be difficult if the olefin was not preactivated. Because the hydrogen affinities of the polar olefins are generally 20 kcal/mol smaller than the corresponding hydride affinities, it is unlikely that the hydride transfer was initiated by hydrogen atom transfer, when the olefins are reduced by hydride donors.

Table 3. Heterolytic and Homolytic Dissociation Energies of C═C π Bond in the Olefins (X) (kcal/mol)

olefins (X)	$\Delta H_{\mathrm{het}}(\pi\ \mathrm{bond})^{a}$	$\Delta H_{\mathrm{hom}}(\pi\ \mathrm{bond})^{b}$	$\Delta H_{\mathrm{hom}}(\pi\ \mathrm{bond}^{\bullet -})^{c}$	$\Delta\Delta H^{d}$	$\Delta\Delta H^{*e}$
1(a–g)					
CH_3O	42.0	42.9	11.9	−0.9	31.0
CH_3	46.7	42.7	12.7	4.0	30.0
H	52.1	42.4	13.9	9.7	28.6
Cl	53.6	42.3	15.4	11.3	27.0
Br	52.5	42.2	15.3	10.3	27.0
CF_3	58.8	42.1	17.9	16.7	24.2
NO_2	61.0	41.7	19.5	19.3	22.1
2(a–g)					
CH_3O	43.0	44.7	17.7	−1.7	27.0
CH_3	47.7	44.5	18.3	3.2	26.2
H	53.0	44.1	19.8	8.9	24.3
Cl	54.5	44.0	21.4	10.5	22.6
Br	53.5	44.0	21.3	9.5	22.8
CF_3	59.7	43.8	23.9	15.9	19.8
NO_2	62.1	43.5	25.6	18.6	17.9
3(a–g)					
CH_3O	44.1	45.2	14.4	−1.1	30.7
CH_3	48.7	44.9	15.3	3.8	29.6
H	54.0	44.5	16.5	9.5	28.0
Cl	55.5	44.5	19.2	11.0	25.3
Br	54.4	44.4	19.0	10.0	25.4
CF_3	60.8	44.3	21.9	16.4	22.5
NO_2	63.3	44.3	24.1	19.0	20.2
4(a–g)					
CH_3O	44.8	46.0	17.9	−1.2	28.2
CH_3	49.6	46.0	18.5	3.6	27.5
H	55.2	45.9	19.5	9.3	26.4
Cl	56.4	45.6	20.7	10.8	24.9
Br	55.4	45.6	20.8	9.8	24.8
CF_3	61.9	45.7	22.5	16.2	23.2
NO_2	64.4	45.6	24.3	18.8	21.3
5(a–g)					
CH_3O	46.6	47.8	18.5	−1.2	29.3
CH_3	51.4	47.6	19.5	3.8	28.2
H	57.0	47.7	20.4	9.3	27.4
Cl	58.4	47.7	22.3	10.7	25.4
Br	57.5	47.8	22.6	9.7	25.1
CF_3	63.4	47.1	25.4	16.3	21.7
NO_2	66.0	47.3	28.1	18.7	19.2
6(a–g)					
CH_3O	48.9	49.5	16.9	−0.6	32.6
CH_3	53. 6	49.3	17.7	4.3	31.6
H	59.0	49.0	18.9	10.0	30.1
Cl	60.6	49.1	20.7	11.5	28.4
Br	59.5	49.0	20.7	10.5	28.3
CF_3	65.7	48.8	23.7	16.9	25.0
NO_2	68.2	48.7	26.6	19.5	22.1
7(a–g)					
CH_3O	51.9	51.7	14.8	0.2	36.9
CH_3	56.7	51.7	16.0	5.0	35.7
H	62.3	51.6	17.7	10.7	34.0
Cl	63.4	51.2	19.7	12.2	31.4
Br	62.3	51.1	19.6	11.2	31.4
CF_3	68.8	51.2	22.9	17.6	28.4
NO_2	71.3	51.2	25.3	20.1	25.9
8(a–g)					
CH_3O	54.2	53.4	14.2	0.8	39.2
CH_3	58.9	53.3	14.9	5.6	38.4
H	64.3	52.9	16.1	11.4	36.8
Cl	65.8	52.9	17.8	12.9	35.1

Table 3. continued

olefins (**X**)	ΔH_{het}(π bond)[a]	ΔH_{hom}(π bond)[b]	ΔH_{hom}(π bond$^{\bullet-}$)[c]	$\Delta\Delta H$[d]	$\Delta\Delta H^{*}$[e]
Br	64.7	52.8	17.7	11.9	35.1
CF_3	71.0	52.7	20.4	18.2	32.3
NO_2	73.3	52.6	22.2	20.7	30.4
9	54.1	46.5	21.0	7.6	25.4
10	54.9	47.5	23.2	7.4	24.3
11	55.2	46.5	26.4	8.7	20.1
12	55.4	45.4	19.6	10.0	25.8
13	56.5	47.3	25.4	9.2	21.9
14	57.2	48.2	23.7	9.0	24.6
15	58.0	48.4	23.7	9.6	24.8
16	59.6	49.6	24.5	10.0	25.1
17	60.0	53.2	22.4	6.8	30.7
18	61.1	49.9	19.2	11.2	30.7
19	61.5	51.1	24.6	10.4	26.5
20	62.2	51.3	20.7	10.9	30.6
21	62.4	51.9	21.4	10.5	30.5

[a] Derived from the equation: ΔH_{het}(π bond) = $\Delta H_{H^-A}(\mathbf{X}) - \Delta H_{H^-A}[(G)PhCH_2^+]$. [b] ΔH_{hom}(π bond) = $\Delta H_{HA}(\mathbf{X}) - \Delta H_{HA}(PhCH_2^\bullet)$. [c] $\Delta H_{hom}(\pi\ bond)^{\bullet-} = \Delta H_{HA}(\mathbf{X}^{\bullet-}) - \Delta H_{HA}(PhCH_2^\bullet)$. [d] $\Delta\Delta H = \Delta H_{het}(\pi\ bond) - \Delta H_{hom}(\pi\ bond)$. [e] $\Delta\Delta H^{*} = \Delta H_{hom}(\pi\ bond) - \Delta H_{hom}(\pi\ bond^{\bullet-})$.

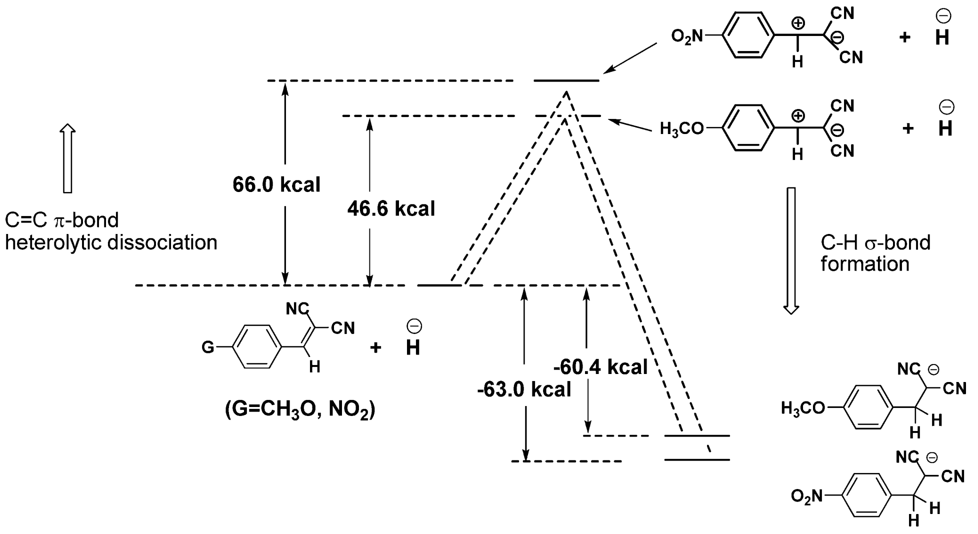


Figure 5. Comparison of potential energy changes for the reductions of olefin **5a** (G = CH_3O) and **5g** (G = NO_2) by hydride anion in acetonitrile.

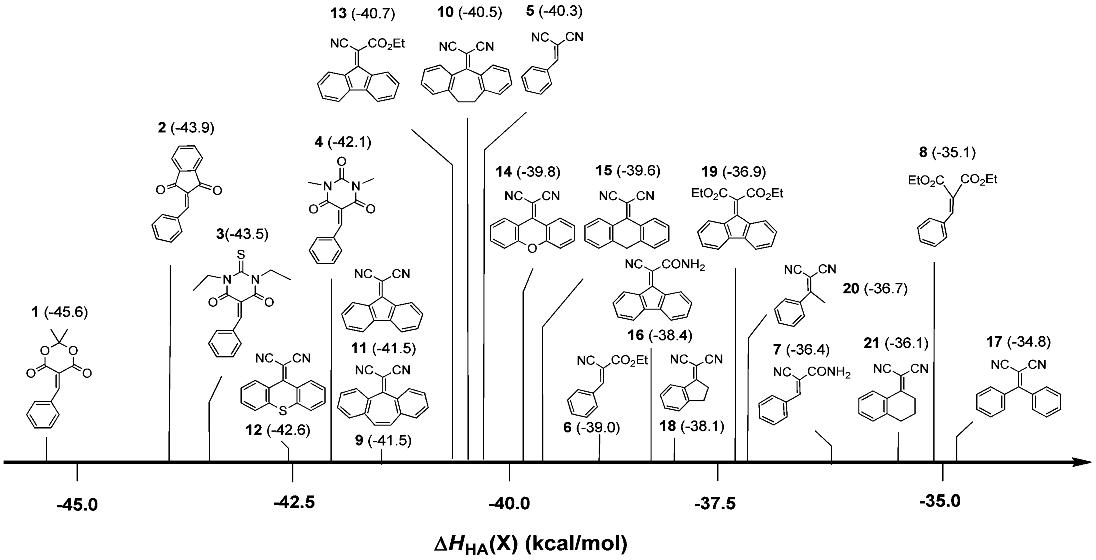


Figure 6. Scale of molar enthalpy change for the 21 typical olefins to capture hydrogen atoms in acetonitrile.

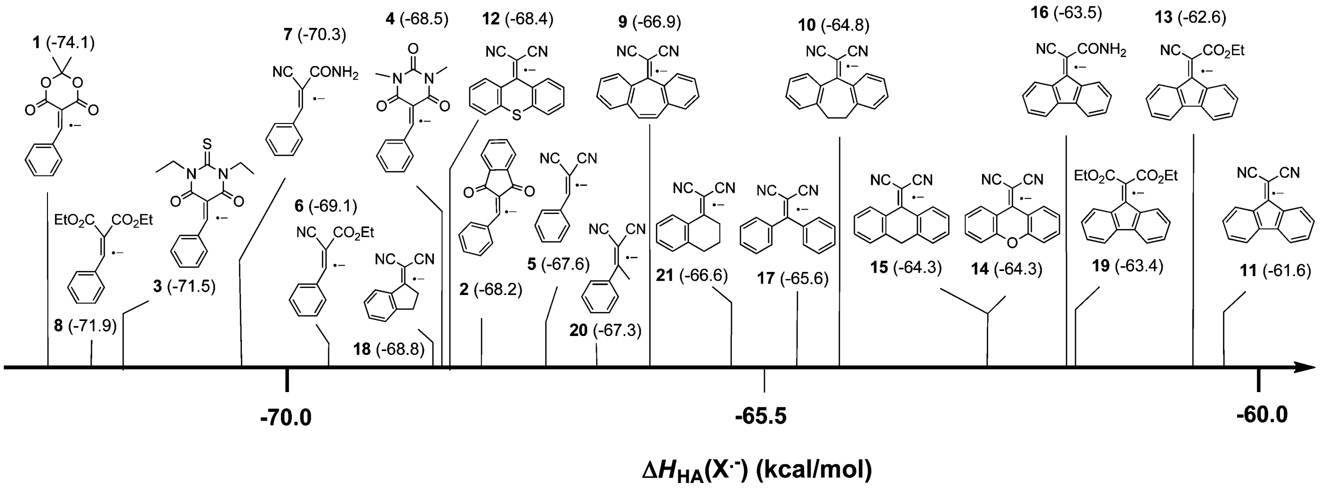


Figure 7. Scale of molar enthalpy change for the radical anions of the 21 typical polar olefins (X$^{\bullet-}$) to capture hydrogen atoms in acetonitrile.

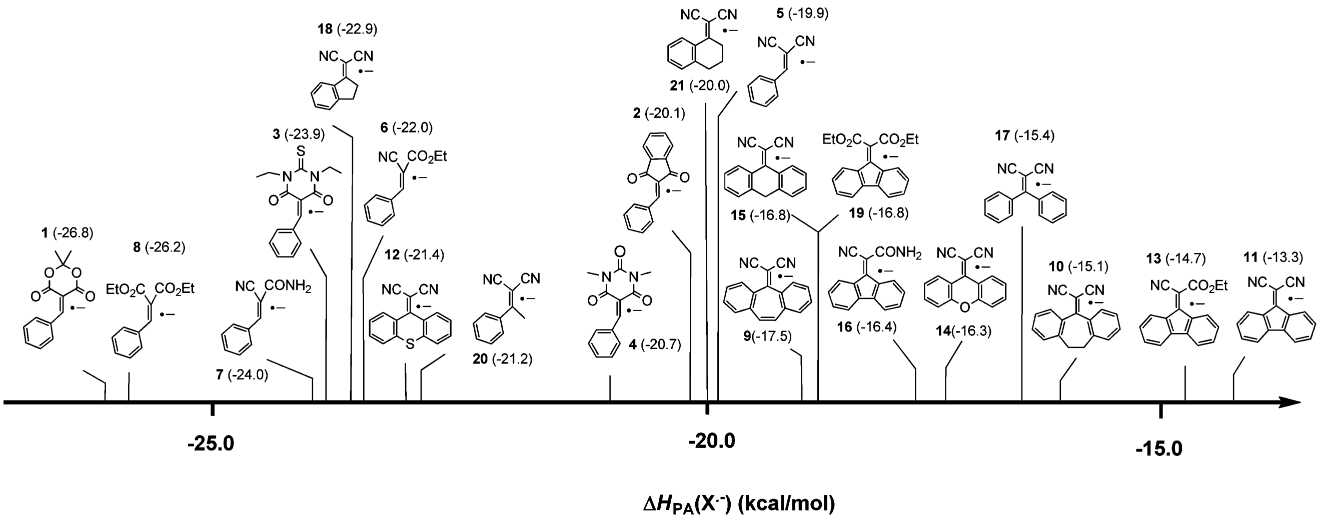


Figure 8. Scale of molar enthalpy change for the radical anions of the 21 typical polar olefins (X$^{\bullet-}$) to capture protons in acetonitrile.

Hydrogen Affinity Scale and Proton Affinity Scale of Radical Anions of the Polar Olefins (X$^{\bullet-}$) in Acetonitrile.

As mentioned in the Introduction, since reductions of polar olefins (X) by hydride donors in solution often take place by initiating of single-electron transfer, the olefins radical anions (X$^{\bullet-}$) as incipient reaction intermediates could be formed, which means that hydrogen affinities and proton affinities of the reaction intermediates (X$^{\bullet-}$) are useful to diagnose the chemical activities of the reaction intermediates and predict the following reaction steps for the reductions of olefins. From columns 4 and 5 in Table 2, we found that the hydrogen affinity scale and proton affinity scale of the olefins radical anions (X$^{\bullet-}$) range from −59.9 to −76.1 kcal/mol and from −10.6 to −29.2 kcal/mol, respectively. If the hydrogen affinities of the olefins radical anions X$^{\bullet-}$ are examined in detail, it is found that, when the substituent is the same (such as G = H), the hydrogen affinities of the olefin radical anions decrease in the order: **1**$^{\bullet-}$ (−74.1 kcal/mol) > **8**$^{\bullet-}$ (−71.9 kcal/mol) > **3**$^{\bullet-}$ (−71.5 kcal/mol) > **7**$^{\bullet-}$ (−70.3 kcal/mol) > **6**$^{\bullet-}$ (−69.1 kcal/mol) > **18**$^{\bullet-}$ (−65.6 kcal/mol) > **4**$^{\bullet-}$ (−68.5 kcal/mol) > **12**$^{\bullet-}$ (−68.4 kcal/mol) > **2c**$^{\bullet-}$ (−68.2 kcal/mol) > **5c**$^{\bullet-}$ (−67.6 kcal/mol) > **20**$^{\bullet-}$ (−67.3 kcal/mol) > **9**$^{\bullet-}$ (−66.9 kcal/mol) > **21**$^{\bullet-}$ (−66.6 kcal/mol) > **17**$^{\bullet-}$ (−65.6 kcal/mol) > **10**$^{\bullet-}$ (−64.8 kcal/mol) > **15**$^{\bullet-}$, **14**$^{\bullet-}$ (−64.3 kcal/mol) > **16**$^{\bullet-}$ (−63.5 kcal/mol) > **19**$^{\bullet-}$ (−63.4 kcal/mol) > **13**$^{\bullet-}$ (−62.6 kcal/mol) > **11**$^{\bullet-}$ (−61.6 kcal/mol) (see Figure 7). Because the hydrogen affinities of X$^{\bullet-}$ are all quite large (generally more negative than −60 kcal/mol), it is conceived that the olefin radical anions X$^{\bullet-}$ are easy for dimerization in acetonitrile.

If the proton affinities of the olefin radical anions (X$^{\bullet-}$) are examined in detail, it is found that, when the substituent is the same (G = H), the proton affinities of the olefin radical anions (X$^{\bullet-}$) decrease in the following order: **1**$^{\bullet-}$ (−26.8 kcal/mol) > **8**$^{\bullet-}$ (−26.2 kcal/mol) > **7**$^{\bullet-}$ (−24.0 kcal/mol) > **3**$^{\bullet-}$ (−23.9 kcal/mol) > **18**$^{\bullet-}$ (−22.9 kcal/mol) > **6**$^{\bullet-}$ (−22.0 kcal/mol) > **12**$^{\bullet-}$ (−21.4 kcal/mol) > **20**$^{\bullet-}$ (−21.2 kcal/mol) > **4c**$^{\bullet-}$ (−20.7 kcal/mol) > **2c**$^{\bullet-}$ (−20.1 kcal/mol) > **21**$^{\bullet-}$ (−20.0 kcal/mol) > **5c**$^{\bullet-}$ (−19.9 kcal/mol) > **9**$^{\bullet-}$ (−17.5 kcal/mol) > **19**$^{\bullet-}$, **15**$^{\bullet-}$ (−16.8 kcal/mol) > **16**$^{\bullet-}$ (−16.4 kcal/mol) > **14**$^{\bullet-}$ (−16.3 kcal/mol) > **17**$^{\bullet-}$ (−15.4 kcal/mol) > **10**$^{\bullet-}$ (−15.1 kcal/mol) > **13**$^{\bullet-}$ (−14.7 kcal/mol) > **11**$^{\bullet-}$ (−13.3 kcal/mol) (see Figure 8), which means that the basicity of olefin radical anions (X$^{\bullet-}$) in acetonitrile are decreased in the following order: **1c**$^{\bullet-}$ > **8c**$^{\bullet-}$ > **7c**$^{\bullet-}$ > **3c**$^{\bullet-}$ > **18**$^{\bullet-}$ > **6c**$^{\bullet-}$ > **12**$^{\bullet-}$ > **20**$^{\bullet-}$ > **4c**$^{\bullet-}$ > **7c**$^{\bullet-}$ > **21**$^{\bullet-}$ > **5c**$^{\bullet-}$ > **9**$^{\bullet-}$ > **19**$^{\bullet-}$, **15**$^{\bullet-}$ > **16**$^{\bullet-}$ > **14**$^{\bullet-}$ > **17**$^{\bullet-}$ > **10**$^{\bullet-}$ > **13**$^{\bullet-}$ > **11**$^{\bullet-}$. Because the proton affinities of the olefin radical anions (X$^{\bullet-}$) are quite large (generally more

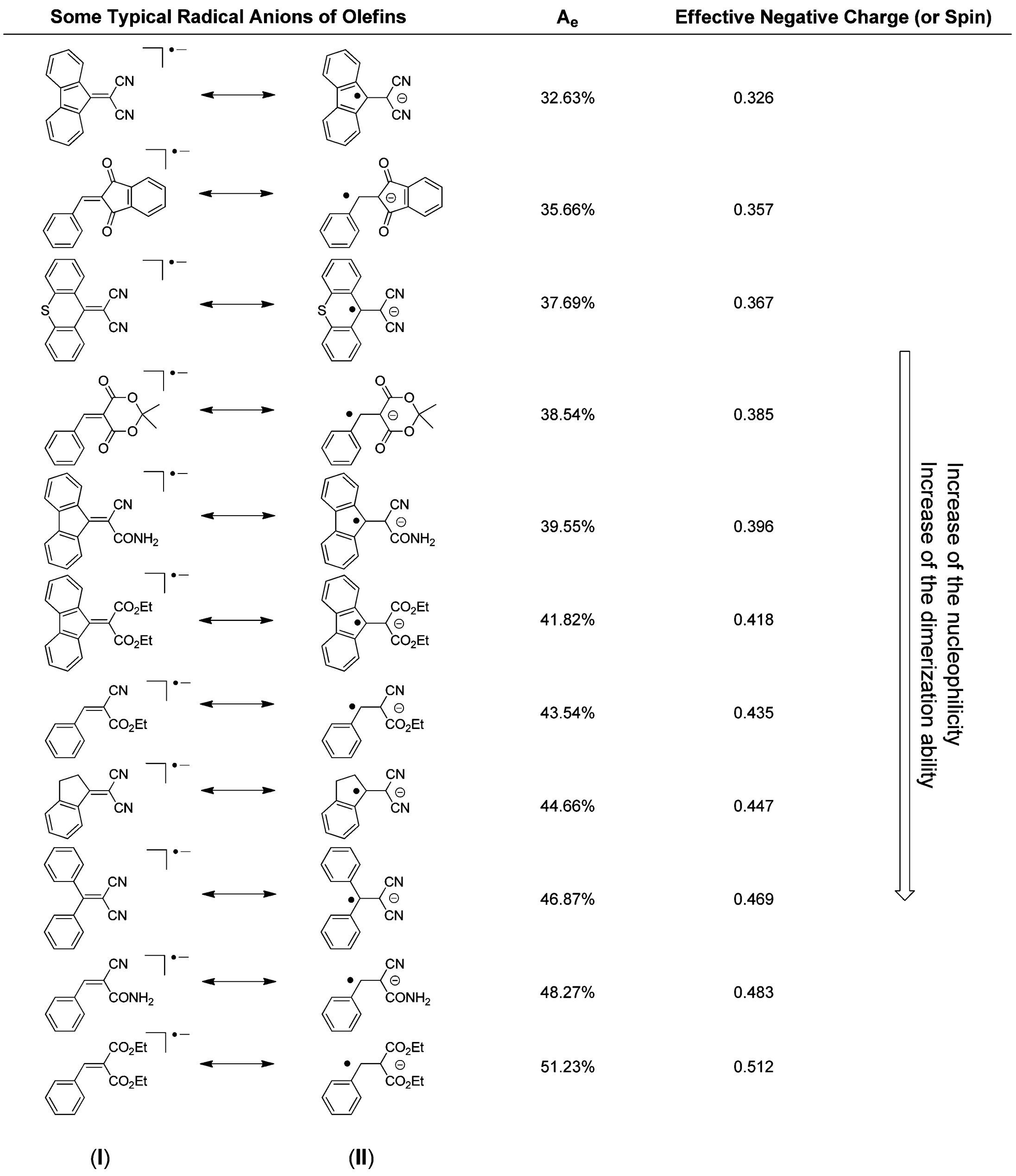


Figure 9. Relative effective negative charge on the center atom for some typical radical anions of olefins; the effective negative charge on the atoms in the delocalized molecular resonance structure herein was defined as zero.

negative than −15.0 kcal/mol), the olefin radical anions are all strong organic bases.

If the hydrogen affinities of the olefin radical anions ($X^{\bullet-}$) were compared with those of the corresponding parent olefins (**X**) (see columns 3 and 4 in Table 2 or Figures 6 and 7), it is found that the hydrogen affinities of the radical anions $X^{\bullet-}$ are generally 20−30 kcal/mol larger than those of the corresponding parent olefins (**X**). Because the value of the hydrogen affinity depends not only on the formation energy of a new C−H σ bond but also on the breaking energy of the old C═C π bond, the term that the differences of the two hydrogen affinities of $X^{\bullet-}$ and **X** is divided by the hydrogen affinities of the radical anions $X^{\bullet-}$ (eq 8) can be used to scale the activation degree (or the weaken degree) of the C═C π bond in the olefins by electron addition. This term, in this work, may be defined as the activation coefficient of the C═C π bond by electron addition (A_e% in eq 8). The detailed activation coefficients of the 69 polar olefins in acetonitrile are summarized in Table 2. As listed in Table 2, when the olefin is **8**(**a**−**g**), the activation coefficient (A_e%) is larger than 50%; when the olefins are **7**, **20**, **17**, and **21**, the activation coefficients (A_e%) are generally larger than 45%, but smaller than 50%; when the olefins are **5**, **6**, **19**, and **18**, the activation coefficients (A_e%) are generally larger than 40%, but smaller than 45%; when the olefins are **2**, **1**, **4**, **3**, **13**, **16**, **9**, **10**, **15**, **14**, and **12**, the π-bond activation coefficients (A_e%) are generally larger than 35%, but smaller than 40%; and when the olefin is **11**, the activation coefficient (A_e%) is smaller than 35%. According to the molecular structure resonance of view,[23] the objective (or natural) structure of $X^{\bullet-}$ could be expressed by several different subjective (or theoretical) resonance structures, such as the idealized Lewis-type structure with the C═C π bond retained

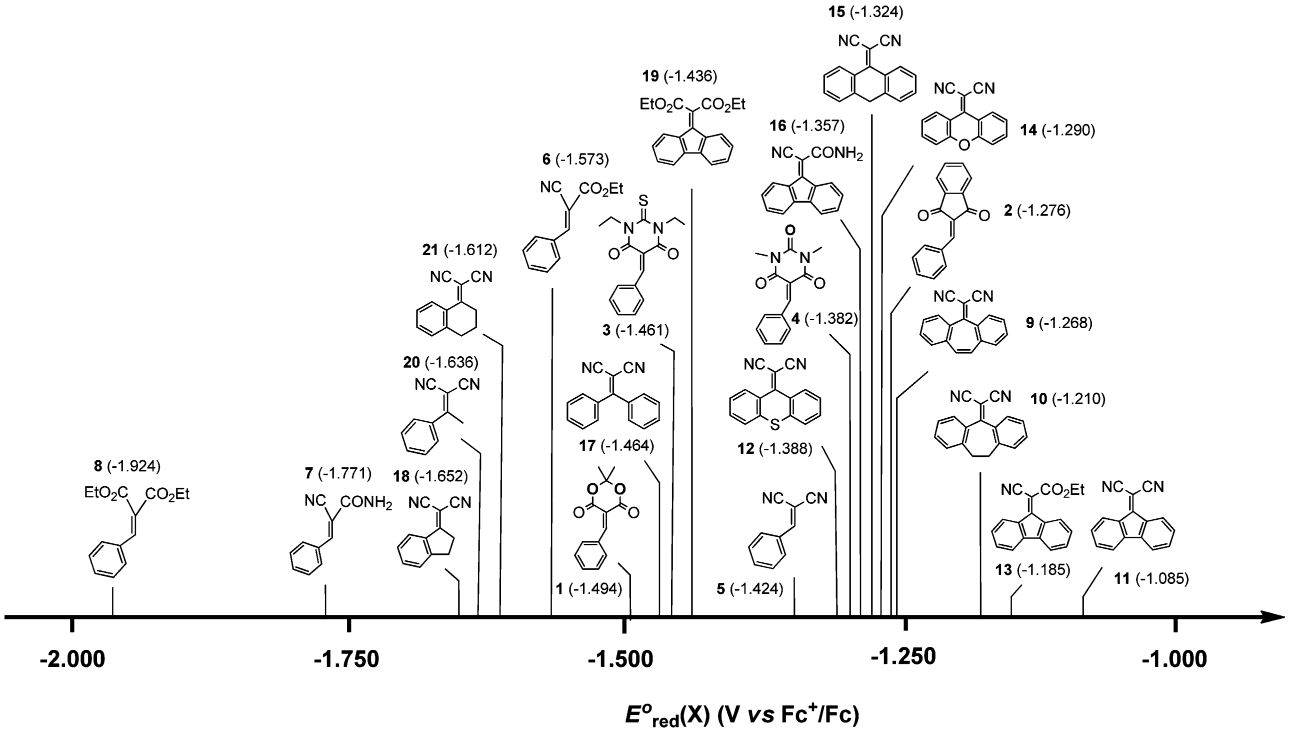


Figure 10. Scale of standard reduction potentials for the 21 typical polar olefins (X) to capture electrons in acetonitrile.

(I), the idealized Lewis-type resonance structure with the C═C π bond broken (II), and some others. Because the resonance structure (II) is merely one efficient (or allowable) Lewis-type structure of $\mathbf{X}^{\bullet-}$ among the resonance structures of $\mathbf{X}^{\bullet-}$ with the C═C π bond broken to accept a proton, it is conceivable that the activation coefficient (A_e%) can scale the percent of the resonance structure (II) of $\mathbf{X}^{\bullet-}$ in the total of the all resonance structures of $\mathbf{X}^{\bullet-}$.

Because the idealized Lewis-type structure with the C═C π bond broken (II) directly expresses the localized state of a single electron and a negative charge in olefin radical anions $\mathbf{X}^{\bullet-}$, A_e% can be used to measure the relative effective negative charge on the molecular negatively charged center atom. Figure 9 shows the relative effective negative charge on the center atom in the olefin radical anions $\mathbf{X}^{\bullet-}$. From Table 2, it is clear that the relative effective negative charge density on the molecular negative charge center atom increases in the order: $\mathbf{11}^{\bullet-} < \mathbf{13}^{\bullet-} < \mathbf{2c}^{\bullet-} < \mathbf{10}^{\bullet-} < \mathbf{12}^{\bullet-} < \mathbf{9}^{\bullet-} < \mathbf{14}^{\bullet-} < \mathbf{15}^{\bullet-}, \mathbf{1c}^{\bullet-}, \mathbf{4c}^{\bullet-} < \mathbf{3c}^{\bullet-} < \mathbf{16}^{\bullet-} < \mathbf{5c}^{\bullet-} < \mathbf{19}^{\bullet-} < \mathbf{6c}^{\bullet-} < \mathbf{18}^{\bullet-} < \mathbf{20}^{\bullet-} < \mathbf{21}^{\bullet-} < \mathbf{17}^{\bullet-} < \mathbf{7c}^{\bullet-} < \mathbf{8c}^{\bullet-}$. It is clear that, for the charged radicals of olefins (in Figure 9), the activation coefficients of the C═C π bond by electron (A_e%) can be used to predict the kinetic driving force of the radical anions of olefins for nucleophilic additions or nucleophilic substitutions, since the nucleophilic additions or nucleophilic substitution rates of the radical anions should be directly dependent on the effective negative charge density on the molecular negative charge center atom. In fact, these predictions have been well-supported by some experimental observations.[24−27]

$$A_e\% = \frac{\Delta H_{HA}(X^{\bullet-}) - \Delta H_{HA}(X)}{\Delta H_{HA}(X^{\bullet-})} \qquad (8)$$

Electron Affinity Scales of the Olefins (X) and the Reduction Intermediate XH$^\bullet$ in Acetonitrile. It is well-known that the standard reduction potentials of olefins (X) and the reduction intermediate $\mathbf{XH}^\bullet$ are very important electrochemical parameters, which can be used as an indicator of the electron-obtaining ability of **X** and $\mathbf{XH}^\bullet$ in thermodynamics. From column 6 in Table 2, it is found that the one-electron reduction potentials of the olefins (**1**−**21**), E^o_{red}(X), range from −0.942 to −2.047 (V vs Fc$^{+/0}$). Since the one-electron reduction potentials of the olefins are quite negative values, generally much more negative than −1.000 V relative to ferrocene, the olefins (**1**−**21**) especially attached by electron-donating groups should be all very weak one-electron acceptors, which suggests that, when the olefins were reduced by hydride donors, the possibility of the electron transfer initiated mechanism is quite small. From column 7 in Table 2, it is clear that the one-electron reduction potentials of the reduction intermediate of olefins ($\mathbf{XH}^\bullet$), E^o_{red}($\mathbf{XH}^\bullet$), range from −0.350 to −0.134 (V vs Fc$^{+/0}$). Since the one-electron reduction potentials of $\mathbf{XH}^\bullet$ are all not too negative values, generally more positive than −0.500 V relative to ferrocene, the reduction intermediate $\mathbf{XH}^\bullet$ should belong to good organic one-electron acceptors, which means that, when the olefins were reduced by hydride donors, if the hydride transfer was initiated by hydrogen atom transfer, the following electron transfer should be quite fast.

To examine the effect of structure of olefins (**X**) and $\mathbf{XH}^\bullet$ on the electron-obtaining abilities, the olefins **X** (**1**−**21**) and $\mathbf{XH}^\bullet$ with the same substituent (e.g., G = H) are ranked in a row according to their one-electron reduction potentials from negative (left) to positive (right) (see Figures 10 and 11, respectively).

Effects of the Remote Substituents on the Thermodynamic Affinities. As shown in Table 2, the hydride affinities, hydrogen affinities, and proton affinities as well as redox potentials of the polar olefins and the related reduction intermediates are not only strongly dependent on the structure of the parent compounds but also strongly dependent on the nature of the remote substituents on the benzene ring.

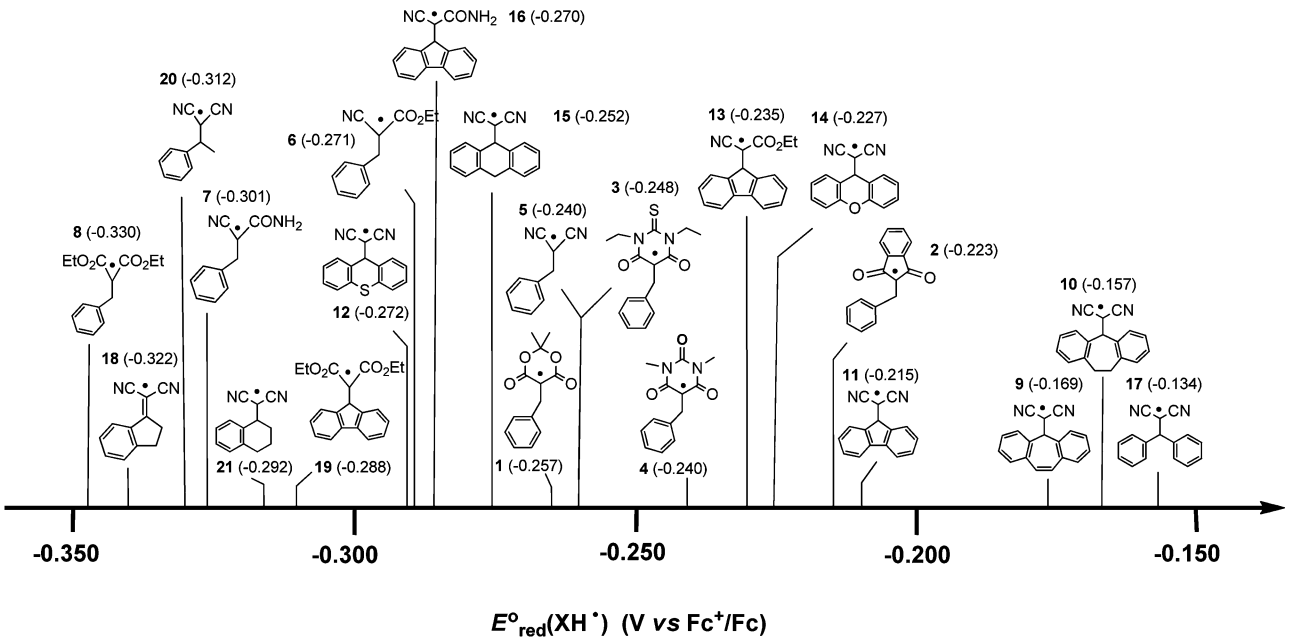


Figure 11. Scale of standard reduction potentials for the hydrogen adducts of the 21 typical polar olefins ($\mathbf{XH^\bullet}$) to capture electrons in acetonitrile.

When the effect of the remote substituent G on the $\Delta H_{\mathrm{H^-A}}(\mathbf{X})$, $\Delta H_{\mathrm{HA}}(\mathbf{X})$, $\Delta H_{\mathrm{PA}}(\mathbf{X^{\bullet-}})$, and $\Delta H_{\mathrm{HA}}(\mathbf{X^{\bullet-}})$ as well as on the $E^{\circ}_{\mathrm{red}}(\mathbf{X})$ and $E^{\circ}_{\mathrm{red}}(\mathbf{XH})$ of olefins **1**−**8** in acetonitrile was examined, it is found that $\Delta H_{\mathrm{H^-A}}(\mathbf{X})$, $\Delta H_{\mathrm{HA}}(\mathbf{X})$, $\Delta H_{\mathrm{PA}}(\mathbf{X^{\bullet-}})$, and $\Delta H_{\mathrm{HA}}(\mathbf{X^{\bullet-}})$ as well as $E^{\circ}_{\mathrm{red}}(\mathbf{X})$ and $E^{\circ}_{\mathrm{red}}(\mathbf{XH^\bullet})$ are all linearly dependent on the Hammett substituent parameters σ with very good correlation coefficients (see the Supporting Information), which means that the Hammett linear free-energy relationships all hold in the six chemical and electrochemical processes. From the slopes and the intercepts of the 48 straight lines, the corresponding 48 mathematical formulas (eqs 9−56) can be easily derived. Evidently, for any substituted polar olefins **X** (**1**−**8**) at the para- and/or meta-position on the benzene ring, it is not difficult to estimate the values of $\Delta H_{\mathrm{H^-A}}(\mathbf{X})$, $\Delta H_{\mathrm{HA}}(\mathbf{X})$, $\Delta H_{\mathrm{PA}}(\mathbf{X^{\bullet-}})$, and $\Delta H_{\mathrm{HA}}(\mathbf{X^{\bullet-}})$, as long as the corresponding Hammett substituent parameters (σ) are available, and the uncertainties of the estimations are generally not more than 0.5 kcal/mol. In the same way, for any substituted polar olefins **X** (**1**−**8**) at the para- and/or meta-position on the benzene ring, the redox potentials $E^{\circ}_{\mathrm{red}}(\mathbf{X})$ and $E^{\circ}_{\mathrm{red}}(\mathbf{XH^\bullet})$ can also be reliably estimated if only the corresponding Hammett substituent parameters are available, and the uncertainties of the estimations are generally not larger than 30 mV. Since the family of the substituent groups is very large, and the Hammett parameters of most substituents located at the para- and meta-position can be easily obtained from the literature,[28] it is evident that the 48 formulas (eq 9−56) should be very useful to predict the related thermodynamic parameters of the polar olefins and their reaction intermediates.

$$\Delta H_{\mathrm{H^-A}}(1) = -2.76\sigma - 65.8 \quad (9)$$

$$\Delta H_{\mathrm{H^-A}}(2) = -2.72\sigma - 64.8 \quad (10)$$

$$\Delta H_{\mathrm{H^-A}}(3) = -2.60\sigma - 63.8 \quad (11)$$

$$\Delta H_{\mathrm{H^-A}}(4) = -2.34\sigma - 62.9 \quad (12)$$

$$\Delta H_{\mathrm{H^-A}}(5) = -2.57\sigma - 61.0 \quad (13)$$

$$\Delta H_{\mathrm{H^-A}}(6) = -2.55\sigma - 58.9 \quad (14)$$

$$\Delta H_{\mathrm{H^-A}}(7) = -2.58\sigma - 55.8 \quad (15)$$

$$\Delta H_{\mathrm{H^-A}}(8) = -2.69\sigma - 53.6 \quad (16)$$

$$\Delta H_{\mathrm{HA}}(1) = -1.02\sigma - 45.5 \quad (17)$$

$$\Delta H_{\mathrm{HA}}(2) = -1.02\sigma - 43.7 \quad (18)$$

$$\Delta H_{\mathrm{HA}}(3) = -0.71\sigma - 43.3 \quad (19)$$

$$\Delta H_{\mathrm{HA}}(4) = -0.43\sigma - 42.1 \quad (20)$$

$$\Delta H_{\mathrm{HA}}(5) = -0.51\sigma - 40.3 \quad (21)$$

$$\Delta H_{\mathrm{HA}}(6) = -0.67\sigma - 38.8 \quad (22)$$

$$\Delta H_{\mathrm{HA}}(7) = -0.61\sigma - 36.5 \quad (23)$$

$$\Delta H_{\mathrm{HA}}(8) = -0.72\sigma - 34.9 \quad (24)$$

$$\Delta H_{\mathrm{HA}}(1^{\bullet-}) = 7.26\sigma - 74.2 \quad (25)$$

$$\Delta H_{\mathrm{HA}}(2^{\bullet-}) = 7.60\sigma - 68.4 \quad (26)$$

$$\Delta H_{\mathrm{HA}}(3^{\bullet-}) = 9.32\sigma - 71.2 \quad (27)$$

$$\Delta H_{\mathrm{HA}}(4^{\bullet-}) = 5.94\sigma - 68.6 \quad (28)$$

$$\Delta H_{\mathrm{HA}}(5^{\bullet-}) = 8.96\sigma - 67.4 \quad (29)$$

$$\Delta H_{\mathrm{HA}}(6^{\bullet-}) = 9.02\sigma - 69.0 \quad (30)$$

$$\Delta H_{\mathrm{HA}}(7^{\bullet-}) = 9.81\sigma - 70.5 \quad (31)$$

$$\Delta H_{\mathrm{HA}}(8^{\bullet-}) = 7.66\sigma - 71.9 \quad (32)$$

$$\Delta H_{\mathrm{PA}}(1^{\bullet-}) = 8.99\sigma - 26.9 \quad (33)$$

$$\Delta H_{\mathrm{PA}}(2^{\bullet-}) = 9.30\sigma - 20.2 \quad (34)$$

$$\Delta H_{\mathrm{PA}}(3^{\bullet-}) = 11.21\sigma - 23.7 \quad (35)$$

$$\Delta H_{\mathrm{PA}}(4^{\bullet-}) = 7.86\sigma - 20.8 \tag{36}$$

$$\Delta H_{\mathrm{PA}}(5^{\bullet-}) = 11.02\sigma - 19.7 \tag{37}$$

$$\Delta H_{\mathrm{PA}}(6^{\bullet-}) = 10.89\sigma - 22.0 \tag{38}$$

$$\Delta H_{\mathrm{PA}}(7^{\bullet-}) = 11.78\sigma - 24.2 \tag{39}$$

$$\Delta H_{\mathrm{PA}}(8^{\bullet-}) = 9.63\sigma - 26.2 \tag{40}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(1) = 0.434\sigma - 1.503 \tag{41}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(2) = 0.447\sigma - 1.291 \tag{42}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(3) = 0.516\sigma - 1.458 \tag{43}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(4) = 0.359\sigma - 1.385 \tag{44}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(5) = 0.499\sigma - 1.413 \tag{45}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(6) = 0.501\sigma - 1.578 \tag{46}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(7) = 0.536\sigma - 1.774 \tag{47}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(8) = 0.448\sigma - 1.931 \tag{48}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(1\mathrm{H}^{\bullet}) = 0.075\sigma - 0.258 \tag{49}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(2\mathrm{H}^{\bullet}) = 0.074\sigma - 0.222 \tag{50}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(3\mathrm{H}^{\bullet}) = 0.082\sigma - 0.248 \tag{51}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(4\mathrm{H}^{\bullet}) = 0.083\sigma - 0.240 \tag{52}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(5\mathrm{H}^{\bullet}) = 0.089\sigma - 0.241 \tag{53}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(6\mathrm{H}^{\bullet}) = 0.081\sigma - 0.270 \tag{54}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(7\mathrm{H}^{\bullet}) = 0.085\sigma - 0.301 \tag{55}$$

$$E^{\mathrm{o}}{}_{\mathrm{red}}(8\mathrm{H}^{\bullet}) = 0.085\sigma - 0.329 \tag{56}$$

■ CONCLUSIONS

In this work, the molar enthalpy changes of 69 typical polar olefins obtaining hydride anions and hydrogen atoms as well as the molar enthalpy changes of their corresponding reaction intermediate ($\mathbf{X}^{\bullet-}$) obtaining protons and hydrogen atoms in acetonitrile were determined or estimated using experimental methods, respectively. The standard reduction potentials of the 69 polar olefins (**X**) and their corresponding hydrogen adducts ($\mathbf{XH}^{\bullet}$) were estimated using CV and OSWV methods, respectively. After examining the determined enthalpy changes and redox potentials as well as the remote substituent effect on the enthalpy changes and the redox potentials, the following conclusions can be made:

(1) For the most polar olefins, especially those attached by weak electron-drawing groups at the α-position, the hydride affinities are all quite small (generally more positive than −66.0 kcal/mol), which means that these olefins all belong to very weak hydride acceptors. If the polar olefins are reduced by some mild organic hydride donors, such as NADH models, BNAH and $\mathrm{AcrH_2}$ in acetonitrile, acids or metal compounds as catalysts are required to break or weaken the C=C π bond in advance.

(2) The hydrogen atom affinities for the 69 polar olefins are all quite small (generally close to or more positive than −45.6 kcal/mol), even smaller than that of $\mathrm{O_2}$ (−48.2 kcal/mol), which means that the 69 polar olefins all belong to very weak hydrogen atom acceptors. If the polar olefins are reduced by some well-known organic hydrogen atom donors, such as $\mathrm{H_2}$, $\mathrm{SnH_4}$, and $\mathrm{(CH_3)_3SiH}$, some catalysts are required to break or weaken the C=C π bond in advance.

(3) The reduction potentials of the 69 polar olefins are generally more positive than −1.000 (V vs $\mathrm{Fc^{+/0}}$), which means that the polar olefins all belong to poor electron acceptors. If the polar olefins are reduced by conventional one-electron chemical reducing agents, such as $\mathrm{SmI_2}$, Fc, and TMPA in acetonitrile, some catalysts are also necessary to increase the ability of the polar olefins to capture electrons.

(4) Because the hydrogen atom affinities of the radical anions of the polar olefins ($\mathbf{X}^{\bullet-}$) are generally much greater than the corresponding proton affinities, the radical anions of the polar olefins ($\mathbf{X}^{\bullet-}$) are likely to form dimers.

(5) Because the electron-accepting ability of the hydrogen adduct of the polar olefins ($\mathbf{XH}^{\bullet}$) is much larger than that of the corresponding parent polar olefins (**X**), it is conceived that, if the reduction of the polar olefins were initiated by electron transfer from a two-electron reducing agent, the second electron transfer could not be in the rate-determined step.

(6) The remote substituent effects hold excellent Hammett linear free-energy relationships on the enthalpy changes of **X** to accept a hydride and hydrogen atom, the enthalpy changes of $\mathbf{X}^{\bullet-}$ to accept a proton and hydrogen atom, as well as the reduction potentials of **X** and $\mathbf{XH}^{\bullet}$, respectively, which means that $\Delta H_{\mathrm{H^-A}}(\mathbf{X})$, $\Delta H_{\mathrm{HA}}(\mathbf{X})$, $\Delta H_{\mathrm{PA}}(\mathbf{X}^{\bullet-})$, and $\Delta H_{\mathrm{HA}}(\mathbf{X}^{\bullet-})$ as well as $E^{\mathrm{o}}{}_{\mathrm{red}}(\mathbf{X})$ and $E^{\mathrm{o}}{}_{\mathrm{red}}(\mathbf{XH})$ of any remotely substituted polar olefins **X** all can be safely estimated from the corresponding Hammett linear free-energy relationship formulas (eqs 9−56), if only the Hammett substituent parameters (σ) are available and the standard derivation of the estimations is less than 0.50 kcal/mol and 30 mV for the enthalpy changes and for the redox potentials, respectively.

It is evident that these important and hard-to-get hydride affinities, hydrogen affinities, proton affinities, and electron affinities of the polar olefins and their related reduction intermediates in acetonitrile, and the conclusions drawn from the effects of the remote substitute, parent structure of polar olefins on the hydride affinities, hydrogen atom affinities, proton affinities, and electron affinities can provide very important clues to examine the electron structure of polar olefins, design the reduction route of the polar olefins, analyze the reaction mechanism, capture the reaction intermediates, predict the reaction direction and tendency, and develop the applications of the polar olefins.

■ EXPERIMENTAL SECTION

Materials. Reagents were commercial quality from freshly opened containers or were purified before use.[29] Reagent grade acetonitrile was refluxed over $\mathrm{KMnO_4}$ and $\mathrm{K_2CO_3}$ for several hours and was doubly distilled over $\mathrm{P_2O_5}$ under argon before use. The commercial tetrabutylammonium hexafluorophosphate ($\mathrm{Bu_4NPF_6}$) was recrystallized from $\mathrm{CH_2Cl_2}$ and was vacuum-dried at 110 °C overnight before preparation of supporting electrolyte solution. 4-Acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium (Ac-tempo^{+}) was synthesized from Ac-tempo,70% $\mathrm{HClO_4}$, and 5.25% NaOCl. The 69 polar olefins

X (**1**−**21** in Scheme 2) were prepared by condensation of the corresponding aldehydes with malononitrile, ethyl α-cyanoacetate, α-cyanoacetamide, diethyl malonate. etc. in the presence of a base, respectively,[30] and were purified by recrystallizing for two times. The corresponding saturated neutral compounds of the polar olefins **X** were obtained from the reduction of **X** by $NaBH_4$ or Hantzsch ester, and the final products were identified by ^{1}H NMR and MS (Supporting Information). The hydride adducts of olefins ($\mathbf{XH}^-$) were prepared according to Arnett's method.[31] The anion precursor (XH_2) was dissolved in dry acetonitrile, and then a slightly excess amount of 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.

Measurements 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 an argon atmosphere at 298 K as described previously.[32] n-Bu_4NPF_6 (0.1 M) in acetonitrile was employed as the supporting electrolyte. A standard three-electrode cell consists of a glassy carbon disk as a working electrode, a platinum wire as a counter electrode, and 0.1 M $AgNO_3$/Ag (in 0.1 M n-Bu_4NPF_6/acetonitrile) as a reference electrode. The ferrocenium/ferrocene redox couple ($Fc^{+/0}$) was taken as the internal standard. The reproducibilities of the potentials were usually $\leqslant$5 mV for ionic species and $\leqslant$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.[33] 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 eight automatic injections from a 250 μL injection syringe containing a standard solution ($\approx$2 mM) into the reaction cell (1.30 mL) containing 1 mL of another concentrated reactant ($\approx$15 mM). The injection volume (5 μL) was delivered at a 0.5 s time interval with 300 s between every two injections. The reaction heat was obtained by integration of each peak except the first.

■ ASSOCIATED CONTENT

Supporting Information

The correlation plots of the six thermodynamic affinities against the Hammett parameters of the remote substituents and the representative ^{1}H NMR spectra of the polar olefins. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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