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Carbon-to-Carbon Identity Proton Transfer from Allene, Ketene, Ketenimine, and Thioketene to Their Respective Conjugate Anions in the Gas Phase. An *ab Initio* Study

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Abstract: Gas-phase acidities of $CH_2{=}C{=}X$ (X = CH_2, NH, O, and S) and barriers for the identity proton transfers ($X{=}C{=}CH_2 + HC{\equiv}C{-}X^- \rightleftharpoons {}^-X{-}C{\equiv}CH + CH_2{=}C{=}X$) as well as geometries and charge distributions of $CH_2{=}C{=}X$, $HC{\equiv}C{-}X^-$ and the transition states of the proton transfer were determined by *ab initio* methods at the MP2/6-311+G(d,p)//MP2/6-311+G(d,p) and B3LYP/6-311+G(d,p) levels of theory. The acidities were also calculated at the CCSD(T)/6-311+G(2df,p) level. A major objective of this study was to examine how the enhanced unsaturation of $CH_2{=}C{=}X$ compared to that of $CH_3CH{=}X$ may affect acidities, transition state imbalances, and intrinsic barriers of the identity proton transfer. The results show that the acidities are all higher while the barriers are lower than for the corresponding $CH_3CH{=}X$ series. The transition states are all imbalanced but less so than for the reactions of $CH_3CH{=}X$.

Introduction

We recently reported a high-level *ab initio* study of the carbon-to-carbon identity proton transfer shown in eq 1, where Y = NO, NO_2, CH=O, CH=NH, CH=S, $CH{=}CH_2$, C≡CH, and CN.[1] Some of the conclusions from that paper which are relevant to the present work can be summarized as follows.

$$Y{-}CH_3 + CH_2{=}Y^- \rightleftharpoons {}^-Y{=}CH_2 + CH_3{-}Y \qquad (1)$$

(1) The acidities of CH_3Y, which range from 390.0 kcal/mol for $CH_3CH{=}CH_2$ to 348.8 kcal/mol for $CH_3CH{=}S$ (MP2/6-311+G(d,p)//MP2/6-311+G(d,p)), are mainly determined by resonance and/or field effects of Y; the polarizability of Y plays an insignificant role, presumably because a large fraction of the anionic charge resides on the Y group rather than on the CH_2 group.

(2) The reactions of eq 1 all have imbalanced transition states in the sense that charge delocalization into the Y group of the incipient carbanion lags behind and charge localization from the Y group onto the CH_2 group of the reactant carbanion is ahead of proton transfer.

(3) The Marcus intrinsic barriers, which range from −9.06 kcal/mol for CH_3CN/CH_2CN^- to 4.18 kcal/mol for $CH_3CH{=}CH_2/CH_2{=}CHCH_2^-$ (MP2/6-311+G(d,p)//MP2/ 6-311+G(d,p)), are all lower than those for the CH_4/CH_3^- system (7.46 kcal/mol), indicating that the stabilization of the transition state by the two Y groups is greater than that of the respective anion by one Y group. This enhanced transition-state stabilization is mainly the result of an exalted field effect by Y on the large negative charge of the CH_2Y fragments caused by the highly positive proton in flight. For the $CH_3CH{=}CH_2/CH_2{=}CHCH_2^-$ system, the field effect is small; here, the polarizability effect on the transition state is the dominant stabilizing factor.

(4) The resonance effect of the Y group leads to a small increase in the barrier because, due to the imbalance, the transition state is not quite as strongly stabilized as the anion. However, the small increase is more than offset by the barrier-reducing field effect of Y and, to a lesser extent, its polarizability effect.

The present paper reports a similar study of eq 2, where X = CH_2, NH, O, and S. There is a similarity between the $H_2C{=}C{=}X/HC{\equiv}C{-}X^-$ systems and the subset of the $CH_3Y/CH_2{=}Y^-$ systems shown in eq 3 (X = CH_2, NH, O, and S), in that the C=X acceptor groups in eq 2 are related to the respective CH=X groups in eq 3. The principal differences are that the acidic carbon in $H_2C{=}C{=}X$ is sp^2 instead of sp^3 hybridized, and the C=X carbon is sp instead of sp^2 hybridized.

$$X{=}C{=}CH_2 + HC{\equiv}C{-}X^- \rightleftharpoons {}^-X{-}C{\equiv}CH + H_2C{=}C{=}X \qquad (2)$$

$$X{=}CH{-}CH_3 + CH_2{=}CH{-}X^- \rightleftharpoons {}^-X{-}CH{=}CH_2 + CH_3{-}CH{=}X \qquad (3)$$

A major objective of this study is to examine how the increased unsaturation/increased s-character may affect intrinsic barriers and transition-state imbalances in reactions 2 compared to reactions 3. This is a question of general and increasing interest[2] because the connection between transition-state imbalances and intrinsic barriers is a dominant factor in determining reactivity in many types of chemical reactions, at least in solution.[5]

Additional motivation for this investigation was provided by some unexpected results reported by Kresge et al.[6] regarding the rates of carbon protonation of ynolate ions such as eq 4.

$$PhC{\equiv}C{-}O^- + H_3O^+ \xrightarrow{k_{H^+} = 1.34 \times 10^{10}\ M^{-1}\ s^{-1}} PhCH{=}C{=}O + H_2O \qquad (4)$$

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[1] Bernasconi, C. F.; Wenzel, P. J. *J. Org. Chem.* **2000**, *66*, 968.

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The rate constant for protonation by H_3O^+ is near the diffusion-controlled limit[7,8] and substantially higher than k_{H^+} for the corresponding enolate ion, PhCH═CH─O⁻ (cis) (3.2×10^7 M^{-1} s^{-1}).[9] In principle, there are two possible explanation for the higher k_{H^+} values in the case of the ynolate ion. (1) The basicity of the carbon of the ynolate ion is much higher than that of PhCH═CH─O⁻. (2) The intrinsic barrier[10] for the protonation of the ynolate ion is lower than that for the enolate ion.

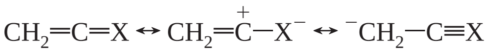
The pK_a value of $PhCH_2CH═O$ is 13.11,[9] but that of PhCH═C═O is not known. However, one may estimate how much higher the pK_a of PhCH═C═O would have to be to account for the entire difference in the k_{H^+} values between ynolate and enolate ion protonation. For the protonation of $CH_2═CH─O^-$ whose pK_a value is 16.73,[11] $k_{H^+} = 1.26 \times 10^9$ M^{-1} s^{-1}.[11] Combined with the k_{H^+} and pK_a values for PhCH═CH─O⁻, one calculates a Brønsted β value of 0.44. Assuming that k_{H^+} or PhC≡C─O⁻ falls on the Brønsted plot defined by $CH_2═CH─O^-$ and PhCH═C─O⁻, one obtains a pK_a of 19.06 for PhCH═C═O, about 6 log units higher than the pK_a of $PhCH_2CH═O$. Such a high pK_a seems unlikely. If ab initio calculations of the gas-phase acidities of $CH_2═C═O$ and $CH_3CH═O$ by Radom et al.[12] can serve as guide, the pK_a values of ketene and acetaldehyde may be very similar to each other, and that would presumably be true for PhCH═C═O and $PhCH_2CH═O$ as well. If this is the case, it would exclude the first explanation and suggest that the main reason for the high k_{H^+} value (eq 4) is a lower intrinsic barrier for ynolate compared to that for enolate ion protonation. A comparison of the gas-phase intrinsic barriers of the $CH_2═C═O/HC≡C─O^-$ system with those of the $CH_3CH═O/CH_2═CH─O^-$ system should provide a more definite answer.

Results and Discussion

The salient structural features of allene, ketene, and ketenimine have been addressed by ab initio calculations before, some at higher levels of theory than in this study.[12,13] Our results,[14] the details of which are summarized in Tables S1 and S2 and Figures S1─S5 of the Supporting Information,[15] are in agreement with these earlier reports. We shall, therefore, focus on those features that are relevant to the questions formulated in the Introduction. Some additional structural features and comments are presented under Methods.

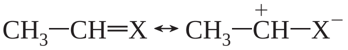
Geometries and Charges. C═C and C═X bond lengths for the neutrals, anions, and transition states obtained at the MP2//MP2 and B3LYP levels are summarized in Table 1. NPA group charges calculated at the same levels are reported in Table 2. A more complete set of geometric parameters is shown in Figures S1─S5,[15] while charges at the RHF level, including Mulliken charges, are reported in Table S2.[15] For the neutral $CH_2═C═X$ molecules and their respective anions, these charges (MP2//MP2 only) as well as some individual atomic charges are also displayed in Chart 1, along with the charges for the $CH_3CH═X/CH_2═CH─X^-$ systems reported recently.[1] The following observations are noteworthy.

(1) Neutral $CH_2═C═X$. As noted before,[13c,h,j] the $CH_2═C═X$ systems are significantly polarized by a shift of negative charge from the C═X to the CH_2 group (e.g., −0.273 on CH_2 of ketene, Chart 1); this contrasts with the negligible polarization of the $CH_3CH═X$ systems (e.g., −0.021 on CH_3 of acetaldehyde, Chart 1). On the other hand, there is less accumulation of negative charge on X in the $CH_2═C═X$ series (e.g., −0.399 on O of ketene, Chart 1) compared to that in the $CH_3CH═X$ series (e.g., −0.493 on O of acetaldehyde, Chart 1). These differences in charge distribution between $CH_2═C═X$ and $CH_3CH═X$ can be attributed to the fact that $CH_2═C═X$ may be described as a resonance hybrid of three canonical structures (**1a**, **1b**, **1c**), while only two resonance structures (**2a**, **2b**) can be written for $CH_3CH═X$. It is **1c** that is responsible for both the accumulation of negative charge on the CH_2 group and the reduction of the negative charge on X relative to that on X in $CH_3CH═X$.



$$CH_2{=}C{=}X \leftrightarrow CH_2{=}\overset{+}{C}{-}X^- \leftrightarrow {}^-CH_2{-}C{\equiv}X^+$$

1a **1b** **1c**



$$CH_3{-}CH{=}X \leftrightarrow CH_3{-}\overset{+}{C}H{-}X^-$$

2a **2b**

The shift in negative charge toward the CH_2 group in $CH_2═C═X$ increases in the order $C═CH_2$[16] < C═S < C═NH

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[2] Only a few of the most recent references are cited here.[3,4]

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[6] Chiang, Y.; Kresge, A. J.; Popik, V. V. *J. Am. Chem. Soc.* **1995**, *117*, 9165.

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[8] The kinetic isotope effect, $k_{H^+}/k_{D^+} = 2.04$,[6] which is greater than expected for a diffusion-controlled proton transfer, suggests that the reaction is still (partially) activation-controlled, and so does the Brønsted plot based on some buffer acids[6] of slope 0.21.

[9] Keeffe, J. R.; Kresge, A. J. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley & Sons: New York, 1990; p 399.

[10] For a nonidentity reaction, the intrinsic barrier is the barrier for a reaction for which $\Delta G^\circ = 0$.

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[14] Some of the results on the ketene reaction have been reported before: Bernasconi, C. F.; Wenzel, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 2430.

[15] See paragraph concerning Supporting Information at the end of this paper.

[16] Allene is, of course, not polarized; the small group charges arise from the fact that the central atom bears a small positive (0.086) charge.

Table 1. Geometries[a]

	neutral	anion	TS	progress at TS (%)
$CH_2{=}C{=}CH_2$				
$r_{C=C}$	1.314 (1.303)[b]	1.281 (1.276)	1.295 (1.286)	
$\Delta r_{C=C}$		−0.033 (−0.027)	−0.019 (−0.017)	57.6 (63.0)
$r_{C=X}$	1.314 (1.303)[b]	1.366 (1.354)	1.342 (1.333)	
$\Delta r_{C=X}$		0.052 (0.051)	0.028 (0.030)	53.8 (58.8)
α	120.9 (121.3)	125.8 (122.4)	123.3 (122.2)	
$\Delta\alpha$		4.9 (1.1)	2.4 (0.9)	49.0[g]
r_{C-H}[c]			1.399	
$CH_2{=}C{=}S$				
$r_{C=C}$	1.322 (1.367)[d]	1.243 (1.228)	1.278 (1.268)	
$\Delta r_{C=C}$		−0.079 (−0.079)	−0.044 (−0.039)	55.7 (49.4)
$r_{C=X}$	1.558 (1.564)[d]	1.662 (1.671)	1.607 (1.616)	
$\Delta r_{C=X}$		0.104 (0.107)	0.049 (0.052)	47.1 (48.6)
α	120.2 (120.7)	169.2 (180.0)	140.0 (134.3)	
$\Delta\alpha$		49.0 (59.3)	19.8 (13.6)	40.4 (22.9)
r_{C-H}[c]			1.354	
$CH_2{=}C{=}NH$				
$r_{C=C}$	1.319 (1.309)[e]	1.275 (1.268)	1.293 (1.284)	
$\Delta r_{C=C}$		−0.44 (−0.041)	−0.026 (−0.025)	59.1 (61.0)
$r_{C=X}$	1.234 (1.222)[e]	1.301 (1.287)	1.272 (1.261)	
$\Delta r_{C=X}$		0.067 (0.065)	0.038 (0.039)	56.7 (60.0)
α	119.9 (120.4)	133.1 (129.5)	125.8 (124.1)	
$\Delta\alpha$		13.2 (9.1)	5.9 (3.7)	44.7 (40.7)
r_{C-H}[c]			1.388	
$CH_2{=}C{=}O$				
$r_{C=C}$	1.322 (1.310)[f]	1.271 (1.253)	1.293 (1.282)	
$\Delta r_{C=C}$		−0.051 (−0.057)	−0.029 (−0.028)	56.9 (49.1)
$r_{C=X}$	1.168 (1.162)[f]	1.229 (1.223)	1.201 (1.195)	
$\Delta r_{C=X}$		0.061 (0.061)	0.033 (0.033)	54.1 (54.1)
α	119.1 (119.7)	141.6 (146.9)	129.7 (127.8)	
$\Delta\alpha$		22.5 (27.2)	10.6 (8.1)	47.1 (29.8)
r_{C-H}[c]			1.374	

[a] MP2/6-311+G(d,p)//MP2/6-311+G(d,p) (B3LYP). [b] Experimental: 1.308 Å (Hirota, E.; Matsamura, C. *J. Chem. Phys.* **1973**, *59*, 3038). [c] H refers to tranferred proton. [d] Experimental: $r_{C=C}$, 1.316 Å, $r_{C=S}$, 1.556 Å (Duncan, J. L.; Jaman, C. N. *Struct. Chem.* **1990**, *1*, 195). [e] Experimental: $r_{C=C}$, 1.292 Å, $r_{C=N}$, 1.242 Å (Kaneti, J.; Nguyen, M. T. *J. Mol. Struct.* **1982**, *87*, 205). [f] Experimental: $r_{C=C}$, 1.316 Å, $r_{C=O}$, 1.161 Å (Duncan, J. L.; Munro, B. *J. Mol. Struct.* **1987**, *161*, 311). [g] The Δα values are too small to yield a meaningful result.

< C═O, indicating that the contribution of the resonance structure **1c** increases in importance in the order C═S < C═NH < C═O. Similar findings have been reported with reference to ketene vs thioketene[13c,j] and interpreted in terms of better π-overlap between the p-orbitals of carbon and oxygen than between carbon and sulfur.

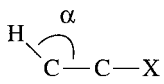
Additional evidence for the importance of resonance structure **1c** can be deduced from a comparison of C═X bond lengths between the $CH_2{=}C{=}X$ and $CH_3CH{=}X$ systems (Table 3). The C═X bonds in $CH_2{=}C{=}X$ are all shorter than those in $CH_3CH{=}X$, which is consistent with a significant contribution of **1c**. However, the percent bond contraction (Table 3) does not give an accurate picture of the situation because the change from sp^2 to sp hybridization of the central carbon increases its electronegativity, a factor that affects the C═X bond length. The operation of this factor is seen in the 2% C═C bond contraction of allene, where no resonance structure **1c** is possible. The bond contraction in this case is the result of the increase in the electronegativity *difference* between the two carbons which strengthen the C═C bond.

For the other $CH_2{=}C{=}X/CH_3CH{=}X$ comparisons, the contribution of the change in hybridization of the central carbon to the change in C═X bond length depends on the electronegativity of X. For the sake of discussion, we shall assume that for S, O, N in the NH group, and C in the CH_2 group as well as the central carbon in $CH_3CH{=}X$, we can use Pauling's electronegativities,[17] while for the central carbon in $CH_2{=}C{=}X$ the electronegativity is 0.3 unit higher.[19] This leads to the electronegativity differences, $\epsilon_C - \epsilon_X$, summarized in Table 3. From the *changes* in $\epsilon_C - \epsilon_X$ that result from converting $CH_3CH{=}X$ to $CH_2{=}C{=}X$, we see that in the case of thioketene the situation is similar to that for allene; i.e., there is again a 0.3 unit increase in the electronegativity difference between C and S. This means that approximately 2% of the 3.7% bond contraction must be attributed to the electronegativity effect, which leaves about 1.7% of the contraction coming from the resonance structure **1c**.[20] For ketenimine and ketene, the situation is reversed because nitrogen and oxygen are more electronegative than carbon; this means that the conversion of $CH_3CH{=}X$ to $CH_2{=}C{=}X$ leads to a 0.3 unit *decrease* in the electronegativity difference and hence to an *elongation* of the C═X bond. If one assumes this elongation to be about 2%,[20] the bond contraction due to the resonance structure **1c** is calculated to be about 5.6% for X = NH and 5.9% for X = O (see last column in Table 3), i.e., much larger than the 1.7% contraction for X = S. This conclusion, which shows that **1c** plays a much larger role for X = O and X = NH than for X = S, is in agreement with that based on charges.

(2) Anions. As will be discussed in the "Acidities" section (below), the main factors stabilizing the anionic charge are the field and resonance (**3b**) effects of the C═X group. Our

$$\underset{\textbf{3a}}{{}^{-}CH{=}C{=}X} \leftrightarrow \underset{\textbf{3b}}{HC{\equiv}C{-}X^{-}}$$

calculations provide several independent parameters for assessing the degree of charge delocalization. They include the C═C bond contraction, C═X bond elongation, the HCC bond angle, α (**4**), and group charges. The changes in these parameters upon



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conversion of $CH_2{=}C{=}X$ to its anion are summarized in Table 4. Also included in the table are the gas-phase resonance substituent constants, σ_R, for the CH═X groups;[21] no σ_R for the C═X groups have been reported, but it seems reasonable to assume that they may, at least qualitatively, follow the trend of $\sigma_R(CH{=}X)$.

The C═C bond contractions, the increase in the HCC bond angle (α), and the amount of charge transfer (χ) all follow the $\sigma_R(CH{=}X)$ values, i.e., $C{=}CH_2 < C{=}NH < C{=}O \ll C{=}S$; the same is essentially the case for the C═X bond elongations, except that for X = NH and O they are virtually the same, with the elongation for NH being just slightly larger than that for O.

It is noteworthy that the changes in the C═X bond length and the amount of charge transfer (χ) are very similar to those obtained in the corresponding $CH_3CH{=}X/{}^{-}CH_2{=}CH{-}X^{-}$ systems (included in Table 4). As was pointed out for these latter systems,[1] the degree of charge delocalization into the π-acceptor

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[17] The Pauling electronegativities are 2.5 (C), 2.5 (S), 3.0 (N), and 3.5 (O).[18]

[18] (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 93. (b) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985; p 14.

[19] The arguments to follow do not depend on exact values of the electronegativities.

[20] It is assumed that equal increments (or decreases) in the electronegativity differences lead to the same percent changes in C═X bond lengths as for allene vs propene.

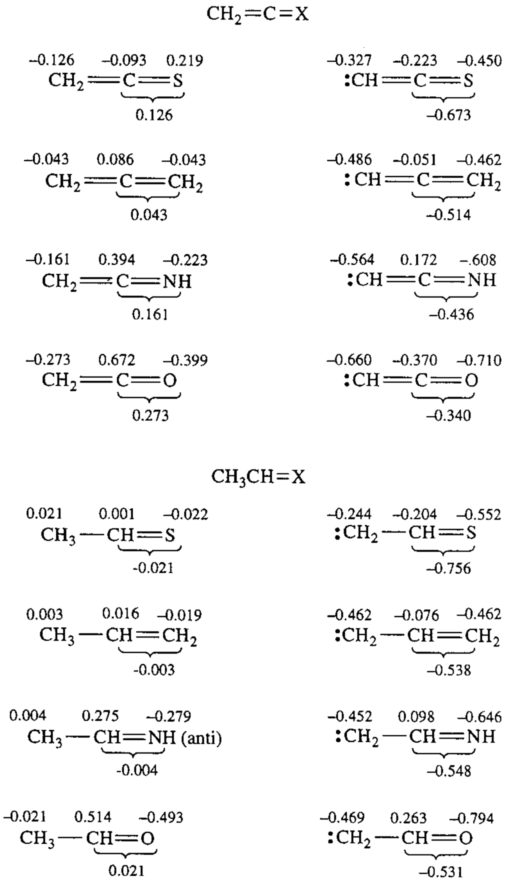
[21] CH═CH$_2$ and CH═O, ref 22; CH═NH and CH═S, estimated in ref 1.

Table 2. Group Charges[a]

group	acid	anion	difference[b]	TS	difference[c]	*n*
			$CH_2{=}C{=}CH_2$			
$CH_2(CH)$	−0.043 (−0.042)	−0.486 (−0.487)	−0.443 (−0.445)	−0.368 (−0.348)	−0.325 (−0.306)[e]	1.29 (1.16)
$C{=}CH_2$	0.043 (0.042)	−0.514 (−0.513)	−0.557 (0.555)[d]	−0.265 (−0.285)	−0.308 (−0.327)[f]	
H in flight				0.266 (0.267)		
			$CH_2{=}C{=}S$			
$CH_2(CH)$	−0.126 (−0.095)	−0.327 (−0.339)	−0.201 (−0.244)	−0.344 (−0.342)	−0.218 (−0.247)[e]	1.43 (1.46)
$C{=}S$	0.126 (0.095)	−0.673 (0.661)	−0.799 (−0.756)[d]	−0.296 (−0.299)	−0.422 (−0.394)[f]	
H in flight				0.280 (0.282)		
			$CH_2{=}C{=}NH$			
$CH_2(CH)$	−0.161 (−0.156)	−0.564 (−0.589)	−0.403 (−0.433)	−0.480 (−0.466)	−0.319 (−0.310)[e]	1.40 (122)
$C{=}NH$	0.161 (0.156)	−0.436 (−0.411)	−0.597 (−0.567)[d]	−0.161 (−0.174)	−0.322 (−0.33)[f]	
H in flight				0.283 (0.280)		
			$CH_2{=}C{=}O$			
$CH_2(CH)$	−0.273 (−0.253)	−0.660 (−0.674)	−0.387 (−0.421)	−0.598 (−0.586)	−0.325 (−0.333)[e]	1.47 (1.42)
$C{=}O$	0.273 (0.253)	−0.340 (−0.326)	−0.613 (−0.579)[d]	−0.051 (−0.060)	−0.324 (−0.313)[f]	
H in flight				0.297 (0.292)		
			$CH_2{=}CH_2$			
$CH_2(CH)$	0 (0)	−0.628 (−0.579)	−0.628 (−0.579)	−0.400 (−0.369)	−0.400 (−0.369)[e]	1.06 (1.05)
CH_2	0 (0)	−0.372 (−0.421)	−0.372 (−0.421)[d]	−0.225 (−0.256)	−0.225 (−0.256)[f]	
H in flight				0.249 (0.249)		
			CH_3CH_3			
$CH_3(CH_2)$	0 (0)	−0.798 (0.770)	−0.798 (0.770)	−0.530 (−0.523)	−0.530 (−0.523)[e]	0.91 (0.88)
CH_3	0 (0)	−0.202 (−0.223)	−0.202 (−0.223)[d]	−0.107 (−0.116)	−0.107 (−0.116)[f]	
H in flight				0.273 (0.278)		

[a] MP2/6-311+G(d,p)//MP2/6-311+G(d,p) (B3LYP). [b] Anion vs acid. [c] TS vs acid. [d] |difference| = χ in eq 5. [e] |difference| = δ_C in eq 5. [f] |difference| = δ_{CX} in eq 5.

Chart 1



group does not follow the electronegativities of X.[23] This is particularly evident when comparing the thioketene with the ketene anion. The reason is that the relative stability of **3b** depends not only on how well the C═X group can support the negative charge but also on how much the C═X double bond strength exceeds that of the C−X single bond. Since the difference in the dissociation energies between these bonds decreases with decreasing electronegativity of X,[24] this factor trends to favor **3b** in the order S > C > N > O. This trend is reflected in the tautomerization enthalpies summarized in Table 5. Thus, the tautomerization of ketene is seen to be much more unfavorable than that of ketenimine and thioketene, and for allene the reaction is actually slightly favorable.

The trend in the tautomerization energies is quite similar to that for the corresponding $CH_3CH{=}X$ (Table 5). However, the extent by which the tautomerization of ketene is disfavored compared to that of the other $CH_2{=}C{=}X$ analogues is much greater than that for acetaldehyde relative to the other $CH_3CH{=}X$ systems. One factor that probably contributes to this state of affairs is the extra stabilization imparted on ketene by the relatively large contribution of the resonance structure **1c**.

With regard to the structure of the anions, an additional factor that favors **3b** for the thioketene anion is the large size of sulfur, which helps in dispersing the negative charge. This explains why charge delocalization into the C═X group is stronger for the thioketene anion than for the ketenimine anion, despite the similar tautomerization energies of thioketene and ketenimine and the lower electronegativity of sulfur compared to that of nitrogen. Finally, it should be noted that the thioketene anion is the only one for which the HCC angle (α) is close to 180° (Table 1), as expected if **3b** is the dominant resonance structure (sp carbon); for the other anions α deviates relatively little from the 120° angle expected if **3a** is the dominant resonance structure (sp^2 carbon).

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[22] Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

[23] However, the individual charges on X (see Chart 1) do follow the electronegativities, as is the case for $^{-}CH_2{-}CH{=}X$.

[24] Average bond energies in kcal/mol: C−S, 65, C═S, 125;[25] C−C, 83, C═C, 146;[26] C−N, 73, C═N, 147;[26] C−O, 86, C═O, 176.[26]

[25] Zhang, X.-M.; Malick, D.; Petersson, G. A. *J. Org. Chem.* **1998**, *63*, 5314.

[26] Streitwieser, A.; Heathcock, C. H.; Kosower, E. M. *Introduction to Organic Chemistry*, 4th ed.; Macmillan: New York, 1992; p 161.

Table 3. Comparison of C═X Bond Lengths ($r_{C=X}$)[a] in CH_2═C═X and CH_3CH═X

C═X	CH_2═C═X	CH_3CH═X[b]	$\Delta r_{C=X}$[c]	bond contraction (%)[d]	CH_2═C═X $\Delta\epsilon^e = \epsilon_C - \epsilon_X$	CH_3CH═X $\Delta\epsilon^e = \epsilon_C - \epsilon_X$	change in $\lvert\Delta\epsilon\rvert$[f]	corrected bond contraction (%)[g]
C═CH_2	1.314	1.341	−0.027	−2.01	0.3	0.0	0.3	−0.00
C═S	1.558	1.618	−0.060	−3.71	0.3	0.0	0.3	−1.70
C═NH	1.234	1.280	−0.046	−3.59	−0.2	−0.5	−0.3	−5.60
C═O	1.168	1.215	−0.047	−3.87	−0.7	−1.0	−0.3	−5.88

[a] MP2/6-311+G(d,p)//MP2/6-311+G(d,p). [b] Reference 1. [c] $r_{C=X}(CH_2{=}C{=}X) - r_{C=X}(CH_3CH{=}X)$. [d] $100 \times (\Delta r_{C=X}/r_{C=X})$. [e] Electronegativities (ϵ): 2.5 (C in CH_2), 2.5 (S), 3.0 (N in NH), 3.5 (O), 2.5 (sp^2 carbon in CH_3CH═X), 2.8 (sp carbon in CH_2═C═X); see text. [f] Change in the absolute electronegativity difference in converting CH_3CH═X to CH_2═C═X. [g] Corrected for electronegativity effects; corresponds to the effect of resonance structure **1c** on the C═X bond.

Table 4. Changes in Bond Length (Δr), Group Charges (χ), and HCC Bond Angles ($\Delta\alpha$) upon Conversion of CH_2═C═X to Its Anion[a]

CH_2═C═X [CH_3CH═X][c]	σ_R (CH═X)	$100 \times \lvert\Delta r_{C=C}\rvert/r_{C=C}$	$100 \times \lvert\Delta r_{C=X}\rvert/r_{C=X}$	charge on C═X in anion	χ[b]	$\Delta\alpha$
CH_2═C═CH_2	0.16	2.51 (2.07)	3.96 (3.91)	−0.514	0.557	4.9 (1.1)
[CH_3CH═CH_2]			[4.33 (4.70)]	[−0.539]	[0.535)	
CH_2═C═NH	≈0.17	3.33 (3.13)	5.43 (5.32)	−0.436	0.597	13.2 (9.1)
[CH_3CH═NH]			[4.77 (5.35)]	[−0.548]	[0.543]	
CH_2═C═O	0.19	3.86 (4.35)	5.22 (5.25)	−0.340	0.613	22.5 (22.2)
[CH_3CH═O]			[4.61 (5.14)]	[−0.531]	[0.552]	
CH_2═C═S	≈0.33	5.98 (6.04)	6.68 (6.84)	−0.673	0.799	49.0 (59.3)
[CH_3CH═S]			[6.67 (7.20)]	[−0.756]	[0.735]	

[a] MP2/6-311+G(d,p)//MP2/6-311+G(d,p) (B3LYP). [b] (charge on C═X)$_{anion}$ − (charge on C═X). [c] Reference 1.

Table 5. Tautomerization Enthalpies (ΔH°_{taut}) and Acidities of the Tautomers ($\Delta H^\circ_{acid,taut}$)[a]

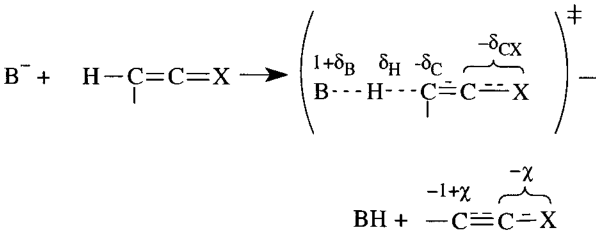
	ΔH°_{taut} (kcal/mol)		$\Delta H^\circ_{acid,taut}$ (kcal/mol)	
C═X	CH_2═C═X	CH_3CH═X[b]	HC≡C−XH	CH_2═CH−XH
C═CH_2	−4.9 (2.1) [−0.7]	0.0 (0.0) [0.0]	385.9 (379.3) [382.0]	390.2 (387.0) [391.2][c]
C═NH	13.0 (17.3) [15.3]	4.9 (2.8) [3.9]	374.3 (375.4) [376.5]	384.2 (375.0) [376.2]
C═O	34.7 (37.5) [34.5]	12.5 (13.4) [10.5]	327.7 (326.5) [332.0]	354.7 (352.3) [356.8]
C═S	13.9 (19.5) [15.5]	3.4 (2.5) [2.4]	331.4 (325.7) [330.8]	345.3 (340.9) [344.8]

[a] MP2/6-311+G(d,p)//MP2/6-311+G(d,p) (B3LYP) [CCSD(T)/6-311+G(2df,2p)]. [b] Reference 1. [c] For CH_3CH═CH_2, the two tautomers are identical, and hence $\Delta H^\circ_{acid,taut} = \Delta H^\circ_{acid}$.

(3) Transition States. Relevant geometric parameters and group charges are summarized in Tables 1 and 2, respectively. A central question is whether the transition states for the reactions of eq 3 are imbalanced, as was found with the corresponding CH_3CH═X/$^-CH_2$═CH−X$^-$ systems and, if so, whether the imbalances are larger or smaller than those for the latter systems. We shall again use the *n* parameter defined in eq 5,[1,27] as a measure of the imbalance; to a first approximation,

$$n = \frac{\log(\delta_{CX}/\chi)}{\log(\delta_C + \delta_{CX})} \tag{5}$$

χ, δ_C, and δ_{CX} can be equated with the partial charges shown in eq 6, although a more precise definition is given in footnotes *d*−*f* of Table 2. Note that eq 5 is simply the logarithmic version of eq 7. For a balanced transition state, $n = 1$; for an imbalanced transition state, where charge delocalization lags behind proton transfer, $n > 1$, with *n* becoming larger with increasing degree of imbalance.



(6)

$$\delta_{CX} = \chi(\delta_C + \delta_{CX})^n \tag{7}$$

Table 6. Transition-State Imbalance Parameters, *n*[a]

C═X	CH_2═C═X	CH_3CH═X[c]
C═CH_2	1.29 (1.16)	1.61 (1.51)
C═NH	1.40 (1.22)	1.55 (1.58)
C═O	1.47 (1.42)	1.52 (1.51)
C═S	1.43 (1.46)	1.42 (1.63)
C[b]	1.06 (1.05)	0.91 (0.88)

[a] MP2/6-311+G(d,p)//MP2/6-311+G(d,p) (B3LYP). [b] CH_2═CH and CH_3CH_3, respectively. [c] Reference 1.

Except for the reactions of ethane and ethene, the *n* values (Table 6) are all significantly larger than unity, but somewhat smaller for the CH_2═C═X than for the CH_3CH═X systems in the case of X = NH, O, and S, and substantially smaller in the case of X = CH_2. As pointed out previously,[1] the factors that determine the size of the imbalance are poorly understood. An early hypothesis, according to which *n* should increase with increasing strength of the π-acceptor group,[4a,28] had to be abandoned[29] in view of results showing that some of the strongest π-acceptors lead to the smallest imbalances.[1] We therefore refrain, at this time, from speculating about why the *n* values for the CH_2═C═X/HC≡C−X$^-$ systems are somewhat lower than those for the corresponding CH_3CH═X/

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[27] (a) Bernasconi, C. F.; Wenzel, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 5405. (b) Bernasconi, C. F.; Wenzel, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 10494.

[28] Saunders, W. H., Jr.; Van Verth, J. E. *J. Org. Chem.* **1994**, *60*, 3452.

[29] We have shown that despite its intuitive appeal, there is no requirement for a correlation between *n* and π-acceptor strength.[27b]

Table 7. Acidities (ΔH°_{acid}) and Barriers ($\Delta H^\ddagger$)

	MP2			B3LYP			CCSD(T)		
C=X	CH_2=C=X	CH_3–CH=X[a]	change[c]	CH_2=C=X	CH_3–CH=X[a]	change[c]	CH_2=C=X	CH_3–CH=X[a]	change[c]
				ΔH°_{taut} (kcal/mol)					
CH_2[b]	407.9	420.2	−12.3	406.3	418.4	−12.1	408.4	420.2	−11.8
C=CH_2	381.1	390.2	−8.9	381.4	387.0	−5.4	383.4	391.2	−7.5
C=NH	374.3	379.8	−5.0	375.4	377.0	−1.6	376.5	380.1	−3.4
C=O	364.4	367.2	−2.9	364.0	363.5	+2.8	366.1	367.3	−3.3
C=S	345.2	348.7	−3.6	345.1	343.4	+1.5	346.3	347.2	−1.0
				$\Delta H^\ddagger$ (kcal/mol)[d]					
CH_2[b]	3.87 (7.02)	4.79 (9.30)	−0.92 (−2.28)	3.44 (4.17)	5.97 (7.67)	−2.53 (−3.50)			
C=CH_2	−3.16 (−0.06)	4.65 (8.22)	−7.81 (−8.28)	−3.01 (−2.51)	5.18 (5.84)	−8.19 (−8.35)			
C=NH	−4.07 (−0.56)	2.90 (6.19)	−6.97 (−6.75)	−5.01 (−4.45)	2.37 (2.99)	−7.38 (−7.44)			
C=O	−7.77 (−4.17)	−0.31 (2.71)	−7.46 (−6.88)	−8.94 (−8.44)	−1.84 (−1.30)	−7.10 (−7.14)			
C=S	−4.52 (−0.61)	0.32 (4.15)	−4.84 (−4.76)	−4.99 (−4.57)	−0.76 (−0.32)	−4.23 (−4.25)			

[a] Reference 1. [b] CH_2=CH_2 and CH_3CH_3, respectively. [c] ΔH°_{acid}(CH_2=C=X) − ΔH°_{acid} (CH_3CH=X) and $\Delta H^\ddagger$(CH_2=C=X) − $\Delta H^\ddagger$(CH_3CH=X), respectively. [d] Numbers in parentheses are corrected for BSSE, see text.

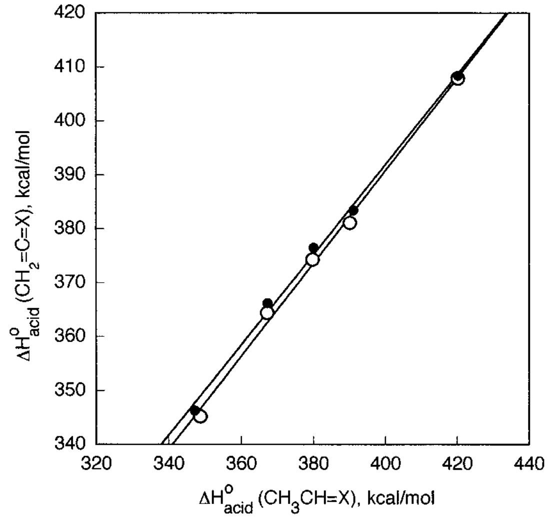

Figure 1. Correlation of ΔH°_{acid}(CH_2=C=X) with ΔH°_{acid} (CH_3CH=X). ○, MP2/6-311+G(d,p)//MP2/6-311+G(d,p) (slope = 0.860 ± 0.31, R^2 = 0.996); ●, CCSD (T)/6-311+G(2df,2p) (slope = 0.836 ± 0.022, R^2 = 0.996). The correlation at the B3LYP level (not shown) yields a slope of 0.796 ± 0.040 (R^2 = 0.992).

CH_2=CH–X^- systems. This is an issue which will be addressed in the future.

For ethene and ethane, $n \approx 1$, because there is no π-bond reorganization or charge delocalization in the carbanion.

Acidities of CH_2=C=X. The acidities of CH_2=C=X (ΔH°_{acid}) are reported in Table 7, along with the acidities of ethane and ethylene. The agreement between the values calculated at different levels is quite good.

A comparison of the acidities of CH_2=C=X with those of the corresponding CH_3CH=X is revealing (Table 7). The CH_2=C=X compounds are all more acidic than their CH_3CH=X counterparts, with a good linear correlation between ΔH°_{acid}(CH_2=C=X) and ΔH°_{acid}(CH_3CH=X) (Figure 1). For ethylene and ethane, the acidity difference is about 12 kcal/mol; the acidity difference for CH_2=C=X versus CH_3CH=X is smaller and decreases with increasing acidity (Table 7), as reflected in the slope of <1 in the plot of Figure 1. Both the higher acidities of CH_2=CH_2 and CH_2=C=X versus CH_3CH_3 and CH_3CH=X, respectively, and the attenuation of the substituent effect in the CH_2=C=X series compared to that in the CH_3CH=X series, must have the same origin. They result from the fact that the anionic carbon in $^-$CH=C=X has more s-character than that in $^-CH_2$CH=X and hence can better support a negative charge; this not only enhances the acidity of the less saturated systems but reduces the dependence on the substituent C=X for its stabilization.

For five members of the CH_3Y family (CH_3CH=CH_2, CH_3CH=O, CH_3NO_2, CH_3NO, and CH_3CN), for which resonance (σ_R), field effect (σ_F), and polarizability effect (σ_α) substituent constants of Y were available,[22] a detailed substituent effect analysis of ΔH°_{acid} was performed, based on a correlation according to eq 8.[1] It yielded $\rho^\circ_F = -43.0$, $\rho^\circ_R = -192.5$, and

$$\Delta\Delta H^\circ_{acid} = \Delta H^\circ_{acid}(CH_3Y) - \Delta H^\circ_{acid}(CH_4) = \rho^\circ_F\sigma_F + \rho^\circ_R\sigma_R + \rho^\circ_\alpha\sigma_\alpha \quad (8)$$

$\rho^\circ_\alpha = -4.64$, indicating that anion stabilization by the field effect and especially the resonance effect are dominant, while the polarizability effect is essentially negligible. We refrain from such an analysis of the CH_2=C=X family because it is unclear whether the σ_F, σ_R, and $\sigma_\alpha$values for CH=X can be applied to C=X and also because the substituent constants for CH=NH and CH=S are somewhat uncertain.[1] Nevertheless, because of the linear correlation between ΔH°_{acid}(CH_2=C=X) and ΔH°_{acid}(CH_3CH=X), it is reasonable to conclude that in the CH_2=C=X series the relative contribution of resonance, field, and polarizability effects to the acidities must be similar to that in the CH_3CH=X series.

Acidities of HC≡C–XH. The acidities of the XH group of HC≡C–XH ($\Delta H^\circ_{acid,taut}$) are compared with those of CH_2=CH–XH in Table 5. Again, the acidities of the more unsaturated systems are higher than those for the more saturated ones, but here the difference in ($\Delta H^\circ_{acid,taut}$) for a given pair *increases* with increasing acidity, at least up to ketene ynol; for the thioketene ynol, the difference is smaller than that for the ketene ynol. The high acidities of HC≡C–XH compared to those of CH_2=C–XH are related to the much larger (positive) enthalpies of tautomerization of the more unsaturated systems (Table 5), coupled with the fact that the CH acidities of CH_2=C=X are only modestly higher than the CH acidities of CH_3CH=X. The particularly high acidity of HC≡C–OH is the result of a particularly high ΔH°_{taut} for tautomerization of ketene.

Barriers. The barriers ($\Delta H^\ddagger$), defined as the difference in enthalpy between the transition state and the *separated* reactants,[30] are summarized in Table 7. The table also includes

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(30) In gas-phase ion–molecule reactions, the transition state is typically preceded by an ion–dipole complex[31] formed between the reactants, and the term "barrier" is sometimes used for the enthalpy difference between the transition state and this ion–dipole complex. These ion–dipole complexes have little relevance to the main focus of this paper (see, e.g., ref 28), and we have not included them in our calculations.

barriers (values in parentheses) that have been corrected for BSSE by the counterpoise method.[32] In view of the controversy about whether the counterpoise method may lead to overcorrection at the MP2 level[33] and the fact that, at a given computational level, the corrections are all very similar for the various reactions, our discussion will focus on the uncorrected values.

There is quite good agreement between the MP2//MP2 and the B3LYP values. Since the MP2//MP2 acidities appear to be more reliable than the B3LYP acidities, we shall assume the same to be true for the barriers and focus the discussion mainly on the MP2//MP2 barriers. The following points are noteworthy.

(1) The barriers for $CH_2{=}C{=}X$ are all lower than those for $CH_2{=}CH_2$. This indicates that the stabilization of the transition state by the two $C{=}X$ groups is greater than the stabilization of the respective anions by one $C{=}X$ group. This is mainly because each of the two $CH{=}C{=}X$ fragments carries more than half a negative charge, so that the total substituent effect of the two $C{=}X$ groups on the transition state is greater than the effect of one $C{=}X$ group on the anion. An additional source of transition-state stabilization is the electrostatic/hydrogen bonding effect between the positively charged proton in flight and the negative $CH{=}C{=}X$ fragments. The situation is quite analogous to that for the $CH_3CH{=}X/^-CH_2{=}CH{-}X^-$ systems,[1] which have lower barriers than the $CH_3CH_3/CH_3CH_2^-$ (Table 7) or CH_4/CH_3^- systems.[34]

(2) The $CH_2{=}C{=}X/HC{\equiv}C{-}X^-$ barriers are lower than the corresponding $CH_3CH{=}X/^-CH_2{=}CH{-}X$ barriers by a constant amount of about 7.5 ± 0.5 kcal for $X = CH_2$, NH, and O, and by ca. 5 kcal/mol for X = S; the difference in $\Delta H^\ddagger$ between ethene and ethane is only about 1 kcal/mol at the MP2//MP2 level, and about 2.5 kcal/mol at the B3LYP level. With respect to the comparison between ketene and acetaldehyde, our results clearly support the notion that the higher k_{H^+} value for the carbon protonation of $PhC{\equiv}C{-}O^{-}$ [6] (eq 4) compared to the protonation of $PhCH{=}CH{-}O^{-}$ [9] is the consequence of a lower intrinsic barrier.

The underlying reason the barriers are lower in the $CH_2{=}C{=}X$ series compared to those in the $CH_3CH{=}X$ series is the same as the reason the acidities of $CH_2{=}C{=}X$ are higher than those of the corresponding $CH_3CH{=}X$, i.e., the greater s-character of the acidic carbon; it allows for more efficient hydrogen-bonding stabilization of the transition state.[35] With regard to the individual differences in $\Delta H^\ddagger$ between $CH_2{=}C{=}X$ and $CH_3CH{=}X$, we may consider the systems with $X = CH_2$, NH, and O ($\Delta\Delta H^\ddagger \approx 7.5$ kcal/mol) as representing "normal" behavior, in which case $CH_2{=}C{=}S$ and $CH_2{=}CH_2$ would represent deviant behavior ($\Delta\Delta H^\ddagger \approx 5$ and 1 kcal/mol, respectively). Our earlier analysis[1] of substituent effects on the barriers for the CH_3Y systems ($CH_3CH{=}O$, $CH_3CH{=}CH_2$, CH_3NO_2, CH_3NO, and CH_3CN) by means of eq 9 can provide some insight into why $CH_2{=}C{=}S$ and $CH_2{=}CH_2$ are deviant. The correlation yielded $\rho_F^\ddagger = -22.6$, $\rho_R^\ddagger = 9.81$, and $\rho_\alpha^\ddagger = 7.59$,

$$\Delta\Delta H^\ddagger = \Delta H^\ddagger(CH_3Y) - \Delta H^\ddagger(CH_4) = \rho_F^\ddagger\sigma_F + \rho_R^\ddagger\sigma_R + \rho_\alpha^\ddagger\sigma_\alpha \tag{9}$$

indicating that the field and polarizability effects[36] lower the barriers, while the resonance effect enhances them. Further analysis revealed that, when combined with the ρ_F°, ρ_R°, and ρ_α° values for the acidities (eq 8), the emerging picture is that the field effect lowers the energy of the transition 1.52[37] times more strongly than that of the anion, the transition-state stabilization by the resonance effect is 0.95[38] times that of the anion stabilization, and there is a significant transition-state stabilization by the polarizability effect.

Just as for the acidities, it is likely that the roles played by the resonance and field effects in affecting the barriers of the $CH_2{=}C{=}X$ systems are similar to those affecting the barriers of the $CH_3CH{=}X$ systems. On the other hand, the polarizabilities of the $C{=}X$ groups are likely to be smaller than those of the corresponding $CH{=}X$ groups because of the greater hardness of the sp carbon in $C{=}X$ compared to that of the sp^2 carbon in $CH{=}X$.[39] Hence, polarizability should have a smaller effect on the barriers in the $CH_2{=}C{=}X$ series. Since σ_α for the $CH{=}S$ group (ca. −0.75)[1] is much larger than that for the other $CH{=}X$ groups (−0.50 for $CH{=}CH_2$,[22] ca. −0.40 for $CH{=}NH$,[1] −0.46 for $CH{=}O$[22]), the transition state of the $CH_3CH{=}S$ reaction benefits disproportionately from the polarizability effect. This is not matched by a comparable effect on the transition state of the $CH_2{=}C{=}S$ reaction, and thus the difference between $\Delta H^\ddagger(CH_2{=}C{=}S)$ and $\Delta H^\ddagger(CH_3CH{=}S)$ is relatively small.

Regarding the small difference between $\Delta H^\ddagger(CH_2{=}CH_2)$ and $\Delta H^\ddagger(CH_3CH_3)$, a similar explanation applies; i.e., some extra stabilization of the transition state of the ethane reaction by the polarizability effect of the methyl group is a likely contributing factor. This notion is supported by the fact that $\Delta H^\ddagger$ for the ethane reaction is lower than that for the CH_4/CH_3^- system.[34] We note, however, that for the fully formed $CH_3CH_2^-$ anion the stabilizing effect of the methyl group is apparently outweighed by a destabilizing factor,[40] as indicated by the slightly lower acidity of ethane compared to that of methane.[34] An additional effect that leads to a reduced $\Delta H^\ddagger(CH_3CH_3)$ is some extra transition-state stabilization because of the larger negative charge on the CH_2 group of the ethane transition state (−0.530, Table 2) compared to that on the CH group of the ethene transition state (−0.400). This allows a stronger electrostatic/hydrogen-bonding interaction with the proton in flight.

Conclusions

(1) The acidities of $CH_2{=}C{=}X$ are higher than the acidities of the corresponding $CH_3CH{=}X$, although the difference in ΔH°_{acid} between the two series decreases with increasing acidity. Both features can be attributed to the greater s-character of the deprotonated carbon in $HC{\equiv}C{-}X^-$ compared to that in $CH_2{=}CH{-}X^-$.

(2) Just as for the $CH_3CH{=}X$ series, the dependence of the acidity on X is dominated by the resonance stabilization of the anion (S > O > NH > CH_2), as reflected in the bond lengths, HCC bond angles, and group charge changes that occur upon

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[34] For the CH_4/CH_3^- system, $\Delta H^\ddagger = 7.46$ (6.12) kcal/mol, while $\Delta H^\circ_{acid} = 418.1$ (415.7) [418.0] kcal/mol.[1]

[35] (a) Cybulski, S. M.; Scheiner, S. *J. Am. Chem. Soc.* **1987**, *109*, 4199. (b) Scheiner, S.; Wang, L. *J. Am. Chem. Soc.* **1992**, *114*, 3650. (c) Scheiner, S. *J. Mol. Struct. (THEOCHEM)* **1994**, *307*, 65.

[36] Because the σ_α values are defined as negative numbers,[22] a negative $\rho_\alpha^\ddagger$ implies a reduction in $\Delta H^\ddagger$ by the polarizability effect.

[37] $1.52 = (\rho_F^\circ + \rho_F^\ddagger)/\rho_F^\circ$, see ref 1.

[38] $0.95 = (\rho_R^\circ + \rho_R^\ddagger)/\rho_R^\circ$, see ref 1.

[39] (a) Pearson, R. G. *Surv. Prog. Chem.* **1969**, *5*, 1. (b) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827.

[40] According to Spitznagel et al.,[41] the reason for the destabilization of $CH_3CH_2^-$ is that the small amount of σ stabilization is outweighed by repulsion between the anion lone pair and the methyl π_{CH_3} orbitals.

[41] Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363.

deprotonation. The greater resonance effect with X = S than with X = O, despite the greater electronegativity of oxygen, is the result of more favorable changes in bond energies in the thioketene case and the large size of sulfur, which helps disperse the negative charge.

(3) The reactions of eq 2 all have imbalanced transition states, with *n* values ranging from 1.29 to 1.47 (MP2//MP2). These *n* values are somewhat smaller than those for the corresponding reactions of eq 3.

(4) The barriers for $CH_2{=}C{=}X$ are all lower than those for $CH_2{=}CH_2$, indicating that the stabilization of the transition state by the two C=X groups is greater than the stabilization of the anion by one C=X group. This is because the sum of the negative charges on the CH=C=X fragments of the transition state is more than unity.

(5) The barriers for the $CH_2{=}C{=}X$ reactions are lower than those for the corresponding $CH_3CH{=}X$ reactions. This is the result of the greater s-character of the acidic carbon, which allows for more efficient hydrogen-bonding stabilization of the transition state of the $CH_2{=}C{=}X$ reactions. The difference in $\Delta H^{\ddagger}$ is relatively large for X = CH_2, NH, and O (ca. 7.5 kcal/mol) but smaller for X = S (ca. 5 kcal/mol) and for $CH_2{=}CH$ vs CH_3CH_3 (ca. 1 kcal/mol). The smaller differences for the latter two systems may be attributed, in part, to a polarizability effect that leads to a stronger reduction of $\Delta H^{\ddagger}$ for the more saturated systems.

(6) Our results support the notion that the higher k_{H^+} value for the carbon protonation of $PhC{\equiv}C{-}O^-$ compared to that for the protonation of $PhCH{=}CH{-}O^-$ is the result of a lower intrinsic barrier.

Methods

Our calculations were performed using the GAUSSIAN 98 suite of programs.[42]

Ketene and Thioketene. The structures for these systems were all calculated from *Z*-matrix inputs. Collinearity of the CCO or CCS atoms was not enforced, and the neutral structures were of C_{2v} symmetry at all levels of theory. Calculation of the anions proceeded from the neutral form minus one hydrogen. A bent ketene anion (both the terminal H and O atoms were nonlinear with respect to the CC atoms) was found to be more stable at MP2. The linear anion was more stable for RHF and B3LYP levels of theory. However, these energy differences are quite small: the electronic energy difference is only 1.13 kcal/mol; with zero-point and thermal corrections the difference is only 0.35 kcal/mol at MP2. At B3LYP the electronic energy favors the bent form by 0.39 kcal/mol; with zero-point and thermal corrections the linear form is favored by 0.36 kcal/mol. Thioketene anion is linear at all levels of theory. A slight bend is observed at MP2: the hydrogen atom deviates by 10.8° and the sulfur by 3.7° from collinearity.

Transition-state structures were constructed with dummy atoms such that the input gave linear CCO or CCS fragments. Slight bends about the central C atom were observed for both transition states at all levels of theory. Rotation about the C−H−C axis of the transferred proton was allowed and was observed for the ketene transition state. Rotation was not observed for the thioketene transition state. The symmetry of the thioketene transition state was C_{2h}, and that of the ketene was C_1.

Ketenimine. The neutral species was constructed using a *Z*-matrix input, such that the CCN atoms were collinear. This was not enforced, and bending of the CCN group was observed. The observed bond was out of the plane defined by the HCH atoms; the lone pair on N appears to cause this distortion. Subsequent optimization from Cartesian coordinates gave the identical geometry. The anion structure was derived from the neutral by replacing an H with a dummy atom. As in the neutral, Cartesian coordinate input gave the same structure as the *Z*-matrix. The CCN fragment was bent in two planes. The transition state was constructed in *Z*-matrix coordinates such that each CCNH coordinate would be identical for each fragment on either side of the transferred proton. The fragments were free to rotate about the axis of the transferred proton. The symmetry of these transition states was C_1.

Allene. In the neutral form the CCC fragment is linear; a dummy atom was used near the central C to ensure this. The *Z*-matrix exploited the S_4 symmetry axis about the central atom. The structure did not change when optimized from the Cartesian coordinates; the resulting structure was of D_{2d} symmetry. The anion was formed by deleting an H from the neutral form. Symmetry about the central atom was broken in optimizing the anion. As in the ketenimine, the anion was bent, the carbanionic carbon bending above the HCH plane. The transition state was constructed with the transferred proton as the center of the inversion for all input parameters. The CCC fragments were constructed to be linear using dummy atoms on each fragment near the central C; the optimized structures showed slight bends at each level of theory. Rotation about the axis of the transferred proton was allowed but not observed. The symmetry of the optimized transition states was C_{2h}.

Zero-Point and Thermal Corrections. Zero-point energies and thermal corrections from the vibrational partition functions[43] were scaled separately using published factors.[44] The partition function was constructed in Microsoft Excel. Contributions from each vibration were totaled over all vibrations. Low-frequency modes ($<$260.0 cm^{-1}) generally corresponded to free internal rotations and their contribution to the zero-point energy is zero; their addition to the thermal correction is $1 \cdot RT$ per mode.

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Supporting Information Available: Tables S1 (energies) and S2 (charges) and Figures S1−S4 (geometries) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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