# Ab Initio Comparison of Identity-Reaction Proton Transfers from Carbon Acids Yielding Localized vs Delocalized Conjugate Bases

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The energy profiles for the identity-reaction carbon-to-carbon proton transfers from representative carbon acids to their respective conjugate bases have been studied by ab initio methods. Calculations at MP2/6-31+G*//6-31+G* and MP4/6-31+G*//MP2/6-31+G* were found to reproduce gas phase acidities well. At the latter level acetaldehyde + acetaldehyde enolate and propene + allyl anion both give high barriers ($\Delta H^{\ddagger}$) relative to the ion–dipole complexes, 16 and 13 kcal mol$^{-1}$, respectively. This is as expected for carbon acids yielding delocalized anions. The barrier for acetonitrile + its conjugate base is much lower, 7 kcal mol$^{-1}$, supporting conclusions from solution studies that there is less delocalization of negative charge into the cyano group than into formally similar unsaturated groups such as carbonyl and vinyl. The barriers ($\Delta H_{TS}$) relative to separated reactants for three acids yielding localized anions, methane, ethylene, and acetylene, decrease linearly with increasing gas-phase acidity. $\Delta H_{TS}$ values for acetaldehyde and propene are well above, and for acetonitrile slightly below, the line defined by these acids. The $\Delta H_{TS}$ values are consistent with experimental results where available. NPA and Mulliken charges support the idea that charge delocalization lags behind proton transfer, but AIM charges do not. The ion–dipole complexes run −1.5 to −14 kcal mol$^{-1}$ ($\Delta H_{well}$) relative to the separated reactants, and their structures are quite variable with type of reactant and level of computation.

## Introduction

It was recently reported that the carbon-to-carbon proton transfer from acetaldehyde to acetaldehyde enolate showed a substantial barrier in ab initio calculations.[1,2] The purpose of the present investigation is to examine identity reaction proton transfers of a representative group of carbon acids yielding delocalized anions and to see how their reaction profiles compare with those of carbon acids yielding localized anions.

Carbon acids yielding delocalized anions have long been useful in synthetic organic chemistry. The fact that they deprotonate much more slowly than oxygen or nitrogen acids of comparable acidity has also attracted the attention of mechanistic chemists. The presently accepted explanation for the existence of a substantial barrier to deprotonation is that charge delocalization of the developing conjugate base in the transition structure lags behind proton transfer, thus depriving the transition structure of at least part of the resonance stabilization enjoyed by the product.[3,4] This basic idea has been further developed by Bernasconi in his principle of nonperfect synchronization (PNS).[5-7] A particularly important advance has been his method for obtaining the intrinsic barrier in solution (the barrier when $\Delta G^\circ = 0$), which removes the contribution of thermodynamic driving force to the barrier and opens the way to discussing the barrier in terms of contributions from charge delocalization, hydrogen bonding, solvation, and polarizability.

The analysis can be further simplified by working in the gas phase and thereby eliminating the contribution of solvation. ICR studies of the deprotonation of a number of carbon acids suggest significant barriers to deprotonation.[8-10] E2 reactions also involve deprotonation accompanied by electronic rearrangement, and a number of anion-promoted eliminations from alkyl halides in the gas phase have been found to be measurably slow.[11,12] Not all gas-phase deprotonations of carbon acids are slow. The reactions of propene and substituted propenes with DO$^-$ result in exchange via multiple proton transfers within the ion dipole complexes, indicating low barriers to proton transfer.[13,14]

Deducing reaction profiles from experimental data requires the use of RRKM theory or other assumptions of uncertain validity. Ab initio calculations on modern computers are capable of reproducing gas-phase acidities with essentially experimental accuracy[15,16] and are thus likely to give reaction profiles that are close to physical reality. Such calculations can aid in the interpretation of experimental data and can also provide details that are as yet inaccessible by experiment.

Ab initio studies of the deprotonation of a number of carbon acids are to be found in the literature, but they are for a variety of reactions and levels of calculation that make systematic comparisons difficult. The most com-

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prehensive set so far is by Scheiner and his co-workers, who examined identity-reaction deprotonations of methane, ethylene, and acetylene by their conjugate bases.[17-19] Methane has also been examined by Gronert at the G2 level.[20] The only published identity reaction calculations on carbon acids yielding delocalized anions are on acetaldehyde[1,2] and acetonitrile.[21] The latter is at a level (4-31G) which, from the findings on acetaldehyde, is unlikely to be quantitatively accurate. A few non-identity reactions have been reported: deprotonation of propene by hydroxide ion at 4-31G,[22] and deprotonation of acetaldehyde by amide, fluoride, and hydroxide ions at 6-31+G.[23] Determining the factors controlling the shapes of reaction profiles for deprotonation of carbon acids thus requires a much more substantial body of calculations at levels that are comparable and high enough to give some confidence in their quantitative accuracy.

## Computational Methods

All of the calculations utilized Gaussian 92.[24] Standard basis sets were used in all cases: 3-21G,[25] 6-31+G*,[26,27] and 6-31+G**.[26,27] Correlation corrections utilized the Møller-Plesset method.[28-32] The enthalpies ($\Delta H_{\mathrm{well}}$, $\Delta H^{\ddagger}$, and $\Delta H_{\mathrm{TS}}$) reported in the tables are corrected to constant pressure and for zero-point-energy differences from 6-31+G*//6-31+G* calculations scaled to 0.9 to account for the overestimation of frequencies by Hartree–Fock methods.[33,34] For species optimized at MP2/6-31+G*//MP2/6-31+G*, frequencies were calculated at that level and ZPE values were scaled to 0.95. The enthalpies were further corrected to 298 K for the contributions of the translational, rotational, and vibrational partition functions.[35] The vibrational contribution is *not* based on scaled frequencies, because inspection of numerous frequency calculations makes it doubtful that low-lying calculated frequencies (the only ones that contribute significantly to the vibrational partition functions) bear a predictable relation to experimental frequencies.[36]

**Table 1. Observed and Calculated Acidities[a] of Carbon Acids**

| acid | $\Delta H$ expt[b] | $\Delta H$ MP2/ 6-31+G*// 6-31+G* | $\Delta H$ MP4/ 6-31+G*// MP2/6-31+G* |
|---|---|---|---|
| $CH_4$ (**4**) | 416.7,[c] 418.0 | 418.2 | 419.4 |
| $C_2H_4$ (**5**) | 406.0, 407.5, 409.4,[c] 407.0 | 407.7 | 408.7 |
| $C_2H_2$ (**6**) | 378.0,[c] 376.7, 379.8, 385.0 | 374.3 | 375.1 |
| $CH_3CH{=}CH_2$ (**3**) | 390.8,[c] 390.3 | 390.3 | 392.5 |
| $CH_3CN$ (**2**) | 372.9,[c] 366.0, 371.8, 369.0 | 373.6 | 375.9 |
| $CH_3CHO$ (**1**) | 365.8,[c] 366.5 | 364.7 | 367.1 |

[a] $\Delta H$ of ionization in kcal mol$^{-1}$. [b] References 16, 37. [c] Judged to be the best value by ref 37.

## Results and Discussion

It is critical for our purposes that all calculations that are to be compared with each other be carried to the same level(s). Our criterion for an acceptable level is the same as in our investigation of the acetaldehyde to acetaldehyde enolate proton transfer:[1] the ability to reproduce experimental values of gas-phase acidities. Table 1 gives results for the acids employed in this study. It is evident that both MP2/6-31+G*//6-31+G* and MP4/6-31+G*//MP2/6-31+G* give acidities within 2–3 kcal mol$^{-1}$ of the experimental[37] values. Neither has a clear advantage over the other, but the higher level is used in most subsequent comparisons.

Identity reactions were chosen so as to eliminate the thermodynamic contributions to the reaction barriers. The reactions involving carbon acids that yield delocalized anions can be described by eq 1.

$$\mathrm{XCH_2^- + HCH_2X = XCH_2H + CH_2X^-} \qquad (1)$$

$$\mathrm{X = CHO\ (\mathbf{1}),\ CN\ (\mathbf{2}),\ CH{=}CH_2\ (\mathbf{3})}$$

Three acids that yield localized anions, methane (**4**), ethylene (**5**), and acetylene (**6**) were also studied. These have been previously calculated by others,[17-20] but were repeated at our levels to ensure strict comparability to results on **1**–**3**.

Energies in hartrees and the zero-point and vibrational energies of the stable species and transition structures involved in the proton transfers are available in the supplementary material. Table 2 gives the relative enthalpies in kcal mol$^{-1}$ of the species involved in the propene to allyl anion proton transfer. All basis sets examined are included so as to illustrate the effect of basis set on the results. For the remainder of the systems studied, Table 3 gives results only at the highest levels. Complete results at all levels are given in the supplementary material.

The well depths ($\Delta H_{\mathrm{well}} = H_{\mathrm{complex}} - H_{\mathrm{reactants}}$) settle down by MP2/6-31+G*//6-31+G* to values that change by no more than 1–2 kcal mol$^{-1}$ at higher levels. Comparisons of **1**–**6** at the common level of MP4/6-

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**Table 2. Enthalpies[a] of Stationary Points in the Propene (3) to Allyl Anion Proton Transfer**

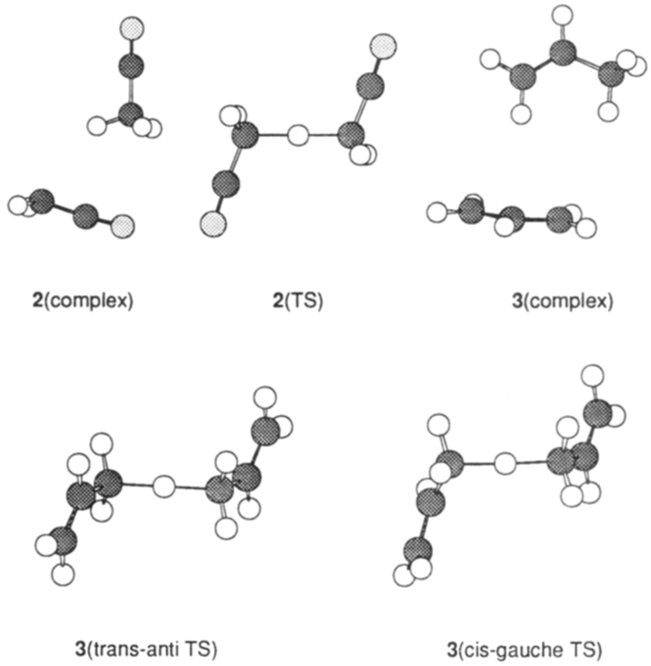
| level | $\Delta H_{\text{well}}$ | $\Delta H^{\ddagger b}$ (trans-anti) | $\Delta H^{\ddagger b}$ (cis-gauche) | $\Delta H_{\text{TS}}{}^{c}$ (trans-anti) | $\Delta H_{\text{TS}}{}^{c}$ (cis-gauche) |
|---|---|---|---|---|---|
| 3-21G//3-21G | −7.8 | 14.3 | 14.8 | 6.5 | 7.0 |
| 6-31+G*//6-31+G* | −1.8 | 22.0 | 22.4 | 20.2 | 20.5 |
| MP2/6-31+G*//6-31+G* | −4.4 | 10.9 | 11.4 | 6.6 | 7.1 |
| MP3/6-31+G*//6-31+G* | −4.2 | 14.0 | 14.4 | 9.7 | 10.1 |
| MP4[d]/6-31+G*//6-31+G* | −4.4 | 11.9 | 12.4 | 7.5 | 8.0 |
| MP2/6-31+G*//MP2/6-31+G* | −5.3 | 11.8 | 12.3 | 6.5 | 7.0 |
| MP3/6-31+G*//MP2/6-31+G* | −4.9 | 15.1 | 15.5 | 10.2 | 10.6 |
| MP4[d]/6-31+G*//MP2/6-31+G* | −5.3 | 13.1 | 13.7 | 7.8 | 8.4 |

[a] In kcal mol$^{-1}$. [b] $H_{\text{TS}} - H_{\text{complex}}$. [c] $H_{\text{TS}} - H_{\text{reactants}}$. [d] MP4SDTQ, frozen core approximation.

**Table 3. Enthalpies[a] of Stationary Points in the Carbon Acid to Conjugate Base Proton Transfer**

| acid, level | $\Delta H_{\text{well}}$ | $\Delta H^{\ddagger b}$ | $\Delta H_{\text{TS}}{}^{c}$ |
|---|---|---|---|
| acetaldehyde[e] (**1**) | | | |
| MP4[d]/6-31+G*//MP2/6-31+G* | −12.8 | 15.8 | 2.9 |
| MP4[d]/6-31+G**//MP2/6-31+G* | −12.9 | 15.0 | 2.1 |
| acetonitrile (**2**) | | | |
| MP2/6-31+G*//MP2/6-31+G* | −14.0 | 6.2 | −7.8 |
| MP4[d]/6-31+G*//MP2/6-31+G* | −14.0 | 7.4 | −6.5 |
| MP4[d]/6-31+G**//MP2/6-31+G* | −13.9 | 6.5 | −7.4 |
| methane (**4**) | | | |
| MP2/6-31+G*//MP2/6-31+G* | −1.4 | 11.2 | 9.8 |
| MP4[d]/6-31+G*//MP2/6-31+G* | −1.5 | 11.9 | 10.4 |
| MP4[d]/6-31+G**//MP2/6-31+G* | −1.6 | 10.5 | 8.9 |
| ethylene (**5**) | | | |
| MP2/6-31+G*//MP2/6-31+G* | −5.2 | 10.4 | 5.2 |
| MP4[d]/6-31+G*//MP2/6-31+G* | −5.2 | 11.4 | 6.2 |
| MP4[d]/6-31+G**//MP2/6-31+G* | −5.2 | 10.1 | 4.9 |
| acetylene (**6**) | | | |
| MP2/6-31+G*//MP2/6-31+G* | −11.1 | 5.7 | −5.4 |
| MP4[d]/6-31+G*//MP2/6-31+G* | −11.0 | 6.2 | −4.8 |
| MP4[d]/6-31+G**//MP2/6-31+G* | −11.0 | 4.5 | −6.5 |

[a] In kcal mol$^{-1}$. [b] $H_{\text{TS}} - H_{\text{complex}}$. [c] $H_{\text{TS}} - H_{\text{reactants}}$. [d] MP4SDTQ, frozen core approximation. [e] Trans-anti TS. Data from ref 1.


**2**(complex) **2**(TS) **3**(complex)

**3**(trans-anti TS) **3**(cis-gauche TS)

**Figure 1.** Ion−dipole complexes and the transition structure in the reaction of acetonitrile (**2**) and propene (**3**) with their conjugate bases.

31+G*//MP2/6-31+G* reveal well depths that vary from −1.5 kcal mol$^{-1}$ for methane to −14.0 kcal mol$^{-1}$ for acetonitrile. The dipole moment of the acid is evidently a strong factor in determining the stabilities of the ion−dipole complexes. Polarizability of the acid and/or the anion is also important, judging from the increasing well depths along the series **4**−**6**. The near equality of the well depths for **3** and **5**, unless it is a simple coincidence, suggests little difference between localized and delocalized anions in the stabilities of their complexes with similar carbon acids.

Structures of the ion−dipole complexes at 6-31+G* for **2** and **3** are given in Figure 1. The structure for **2** is best characterized as tail-to-tail (anion α-carbon to acid α-carbon). The complex for **3** shows the allyl anion lined up under the propene. For both **2** and **3** the ion−dipole complexes are in an orientation such that relatively little geometric change is needed to initiate bonding between the α-carbon of the anion and an α−hydrogen of the acid. This contrasts with the case of **1**, where a a head-to-tail (enolate oxygen to α-carbon of acetaldehyde) complex (Figure 1 of ref 1) must reorient to a tail-to-tail species before proton transfer can commence. Another difference with **1** is that the complexes for **2** and **3** change little with level of calculation.

Although the ion−dipole complexes are well-defined stable species by the criterion of possessing no imaginary frequencies, changing the relative orientations of the components results in only slight variations in energy. All of them have numerous very low-lying vibrational frequencies corresponding to relative motions of the components. Any reorientation needed for proton transfer to occur can thus easily be achieved at thermal energies in these highly fluxional systems.

The transition structures for **1**−**3**, unlike the ion−dipole complexes, all have extended arrangements with linear or nearly linear C- - -H- - -C partial structures (Figure 1 of ref 1 gives the structures for **1**). Both **1** and **3** have two transition structures, trans-anti and cis-gauche. The trans and cis arrangements are defined by whether the oxygens (**1**) or terminal carbons (**3**) are on the opposite (trans) or the same (cis) side of the plane defined by the four carbon atoms and the hydrogen in transit when both structures are stretched into the anti conformation, while anti and gauche refer to conformations about the C- - -H- - -C axis. In each case there is only a few tenths of a kcal difference in the enthalpies of the two transition structures. Interestingly, the cis-gauche structure is more stable for **1** but the trans-anti for **3**. In spite of the trivial difference in energies, the two transition structures are not expected to be easily interconvertible, for rotation about a partial double bond is required.

One would intuitively expect the single transition structure for **2** to be little changed in energy by rotation about the C- - -H- - -C axis. A brief investigation of the anti vs. syn periplanar structures did reveal only a 2.3 kcal mol$^{-1}$ rise in energy for the latter relative to the former when the dihedral angle was fixed and all other

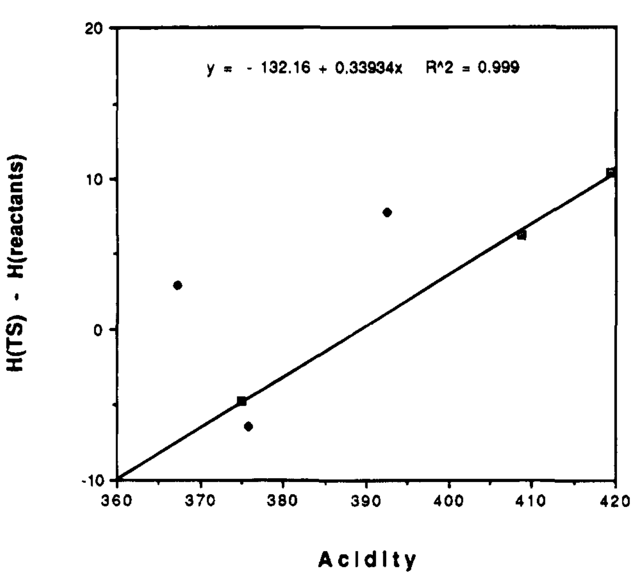


**Figure 2.** Plot of H(TS) − $H$(reactants) (= $\Delta H_{TS}$) for identity-reaction proton transfers vs acidity (kcal $mol^{-1}$). Points on line: acetylene, ethylene, and methane. The least-squares fit is for these three points. Points above line: acetaldehyde and propene. Point below line: acetonitrile.

parameters optimized at 6-31+G*. This difference rose to a much more imposing 13.0 kcal $mol^{-1}$, however, when an MP4 single-point correction was applied. An even larger increase, 14.6 kcal $mol^{-1}$, was found (also at MP4/6-31+G*//6-31+G*) when the C- - -H- - -C angle was reduced from 180° to 150°. This observation provides at least a partial explanation of the increase in energy with reduction of the dihedral angle: the optimized C- - -H- - -C angle in the syn conformation is reduced to 167.5° from the 180° of the anti conformation.

The enthalpies of activation relative to the ion−dipole complexes, $\Delta H^{\ddagger}$, listed in Table 2 are consistently high at 6-31+G*//6-31+G* compared to the values obtained at correlated levels. The 3-21G//3-21G values are closer to those at correlated levels, presumably due to fortuitous cancelation of errors. Once the Møller−Plesset corrections are introduced, $\Delta H^{\ddagger}$ remains within a range of a few kcal regardless of the level or of whether optimization was at 6-31+G* or MP2/6-31+G*. The same pattern is found for the systems listed in Table 3 (see supplementary material, Table S-4). Comparing the values for **1**−**6** at the common level of MP4/6-31+G*//MP2/6-31+G*, **1** and **3** clearly stand out as having the highest barriers, though **4** is not far behind.

It has been pointed out before that barriers tend to be lower the greater the acidity of the proton donor.[18] When there is considerable structural change, however, even a qualitative relationship between $\Delta H^{\ddagger}$ and $\Delta H_{acid}$ breaks down. The barriers for **1** and **4**, the strongest and weakest acids, respectively, are within 4 kcal of each other, and a plot of $\Delta H^{\ddagger}$ vs $\Delta H_{acid}$ shows little but scatter. This is not surprising, for $\Delta H^{\ddagger}$ is the difference in enthalpy between the ion−dipole complex and the transition structure. The enthalpy of the ion−dipole complex is determined largely by attractive forces between the components which bear no necessary relation to the stability of the transition structure or to the acidity of the proton donor.

In contrast, a plot of $\Delta H_{TS}$ ($H_{TS} - H_{reactants}$) vs $\Delta H_{acid}$ for **4**−**6** (Figure 2) defines an excellent straight-line relation of slope 0.34. Kreevoy[38] has pointed out that the slope of such a line should be a measure of the charge on the proton in transit, and it is close to the NPA charges on that proton (0.28−0.31) for these three substrates. Points for **1** and **3** are well above the line, as would be expected if acids yielding delocalized anions had unusually high barriers. Since $\Delta H_{TS}$ is the difference in enthalpy between the separated reactants and the transition structure, it is independent of the specific factors which determine the stabilities of the ion−dipole complexes. The observed rate and efficiency thus depend directly on $\Delta H_{TS}$ because it is the difference between the barrier to proton transfer, $\Delta H^{\ddagger}$, and the barrier, $-\Delta H_{well}$, for return to reactants from the ion−dipole complex. The proton transfer involves a tighter transition structure than the return to reactants, so that the latter will be preferred on entropic grounds even when the enthalpic barriers are equal.

The $\Delta H_{TS}$ value for **2** is anomalous in the sense that the conjugate base of acetonitrile is in principle capable of charge delocalization from carbon to nitrogen. On this basis one would expect **2** to deprotonate more slowly than an acid of comparable acidity yielding a localized anion. Instead, the point for **2** is slightly *below* the line defined by **4**−**6**. This observation ties in with substantial evidence in the literature that the inductive effect of the cyano group relative to its resonance effect is of much more importance in stabilizing an adjacent negative charge than is the case for formally similar unsaturated groups such as carbonyl and vinyl. Although there is some delocalization in the cyanomethyl anion, it is less than that in acetaldehyde enolate.[39] Structures of the cyanomethyl anion optimized at 6-31+G* and above are pyramidal, unlike the planar acetaldehyde enolate, though the barrier to inversion is quite low. Cyanocarbon acids give Eigen plots reminiscent of those for acids that deprotonate at a diffusion-controlled rate, although with the important difference that the maximum rate is several orders of magnitude lower.[40] Crystal structures show little change in the carbon−nitrogen bond length between nitriles and their conjugate bases.[41,42] $^{13}C$ NMR shifts are claimed to show little delocalization in conjugate bases of cyanocarbon acids.[43]

Our $\Delta H_{TS}$ value for **2** is consistent with all of this evidence except for the fact that its point is definitely *below* the line rather than slightly above it, as would be expected for even minor delocalization in the cyanomethyl anion. This discrepancy could be explained if the polarizability of the cyano group stabilizes the transition structure slightly more than incomplete delocalization destabilizes it.[44]

Although the levels we have employed in our calculations reproduce quite satisfactorily the gas-phase acidities of **1**−**6**, there remains the question of whether

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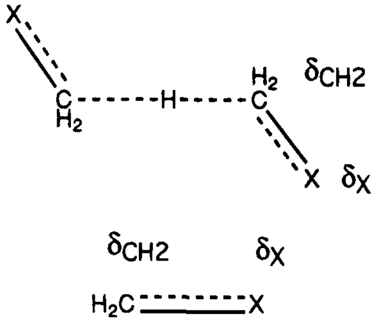
**Table 4. Comparisons with Experiment**[a]

| acid | $\Delta H_{TS}$(calcd),[b] kcal mol$^{-1}$ | $k \times 10^{10}$ (obsd), cm$^3$ molecule$^{-1}$ s$^{-1}$ | efficiency ($k/k$(ADO)[c]) |
|---|---|---|---|
| $CH_3CH{=}CH_2$ | 7.8 | <0.001 | <0.0001 |
| $C_2H_2$ | −4.8 | 3.52 ± 0.14 | 0.30 |
| $CH_3CN$ | −6.5 | 5.92 ± 0.15 | 0.20 |

[a] Unpublished results of G. E. Davico and C. H. DePuy. [b] MP4/6-31+G*//MP2/6-31+G*. [c] $k$(ADO) is the encounter rate calculated by the average dipole orientation method.

**Scheme 1**



equivalent accuracy is achieved for all features of the reaction profiles. Proceeding from reaction profiles to calculated rates is not a simple and straightforward process, nor is the converse, deducing reaction profiles from experimental rates. Nonetheless, it is usually possible to state whether a given reaction profile is consistent with experimental data. Table 4 presents rates and efficiencies for three of our identity reactions. These figures are from experiments in a flowing afterglow apparatus performed by isolating the natural-abundance $^{13}C$ anions and observing their decay.[45] The table also includes our $\Delta H_{TS}$ values for comparison. The deprotonation of propene is too slow to measure, as expected for a barrier to deprotonation that is well above the separated reactants. Measurable rates and efficiencies are obtained for both acetylene and acetonitrile. The rate for the latter is faster because the barrier is farther below the separated reactants than is the case for the former. Our results are thus seen to be entirely consistent with the experimental data, at least in a qualitative sense.

Why the efficiency is lower for acetonitrile than for acetylene is not clear, though the difference is not large enough to be a cause for major concern. It may be that the entropic advantage for return to reactants is greater for acetonitrile. A possible source of an entropic difference is that the acetonitrile complex gains three degrees of rotational freedom on dissociation, while the linear acetylene complex gains only two.[46] Another possibility is that $k$(ADO), which is calculated, not measured, is inaccurate in one or both cases.

We turn next to the question of whether there is incomplete delocalization of charge in the transition structure relative to the product anion. For this purpose we compare the charge on the α-methylene group, $\delta_{CH_2}$, to the charge on the group X (CHO, CN, or $CH{=}CH_2$), $\delta_X$, in the transition structure relative to the product conjugate base. Table 5 shows these quantities calculated from NPA (natural population analysis) charges.[47,48]

**Table 5. Group Charges (NPA) at MP2/6-31+G***

| species | α-$CH_2$ | X | α-$CH_2$/X | TS/$CH_2X^-$ |
|---|---|---|---|---|
| | | CHO | | |
| $C_4H_7O_2^-$ TS[a] | −0.450 | −0.219 | 2.055 | |
| $CH_2CHO^-$ | −0.506 | −0.495 | 1.022 | 2.01 |
| | | CN | | |
| $C_4H_5N_2^-$ TS | −0.473 | −0.201 | 2.353 | |
| $CH_2CN^-$ | −0.660 | −0.340 | 1.941 | 1.21 |
| | | $CH{=}CH_2$ | | |
| $C_6H_{11}^-$ TS[a] | −0.445 | −0.219 | 2.032 | |
| $CH_2CHCH_2^-$ | −0.516 | −0.490 | 1.053 | 1.93 |

[a] Trans-anti.

**Table 6. Group Charges (AIM) at MP2/6-31+G***

| species | α-$CH_2$ | X | α-$CH_2$/X | TS/$CH_2X^-$ |
|---|---|---|---|---|
| | | CHO | | |
| $C_4H_7O_2^-$ TS[a] | −0.261 | −0.414 | 0.630 | |
| Enolate | −0.410 | −0.589 | 0.696 | 0.91 |
| | | CN | | |
| $C_4H_5N_2^-$ TS | −0.031 | −0.668 | 0.046 | |
| Anion | −0.150 | −0.849 | 0.177 | 0.26 |
| | | $CH{=}CH_2$ | | |
| $C_6H_{11}^-$ TS[a] | −0.306 | −0.366 | 0.836 | |
| anion | −0.449 | −0.550 | 0.816 | 1.02 |

[a] Trans-anti.

Taking the ratio of $\delta_{CH_2}/\delta_X$ in the transition structure to $\delta_{CH2}/\delta_X$ in the product (last column) displays most clearly whether there is a lag in charge delocalization. There are substantial lags for acetaldehyde and propene and a significant though much smaller lag for acetonitrile. The NPA charges are thus entirely consistent with the principle of nonperfect synchronization[5−7] and with the idea that delocalization is less important in cyanocarbanions than in enolates or allylic carbanions. Mulliken charges give numerically different results, but the qualitative conclusions are the same.

To explore further the role of charge distribution, atoms in molecules (AIM) charges were also calculated.[49−51] These results are given in Table 6. Surprisingly, they present a completely different picture from the NPA charges. In two of three cases, there appears to be a *depletion* of charge at the methylene group in the transition structure relative to the conjugate base product. In the third case, propene, there is only a trivially small excess of charge in the transition structure methylene group. The substantial depletion of charge at the transition structure methylene group in the case of acetonitrile is particularly puzzling. To explore the possibility that the expected $\pi$ electron shifts are masked by opposite $\sigma$ electron shifts,[52−54] an attempt was made in the case of acetaldehyde to distinguish between the two. Although acetaldehyde enolate has cleanly separated $\sigma$ and $\pi$ orbitals, the mixed character of many orbitals of the transition structure precluded an effort to examine $\sigma$ and $\pi$ electron shifts separately.

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Another puzzling feature of the AIM charges is the charge distribution in the anions. The NPA charges show the negative charge approximately equally distributed between the methylene group and the group X for acetaldehyde enolate and allyl anion, but nearly twice as much charge on the methylene group as on the cyano group in the cyanomethyl anion. This is just as expected from experimental and computational evidence that delocalization in the cyanomethyl anion is relatively limited (vide supra). The AIM group charges do not differ greatly from the NPA results for acetaldehyde enolate and allyl anion, but show most of the negative charge of the cyanomethyl anion to be in the cyano group, suggesting much greater delocalization in the cyanomethyl anion than in the other two. This is precisely the reverse of expectations based on experiment and on other computational results.

Taken at face value, the AIM charges contradict the principle of nonperfect synchronization. Serious difficulties arise, however, when the AIM charges are assumed to better represent physical reality than the NPA or Mulliken charges. If charge transfer from the base and charge reorganization are approximately synchronized for **1** and **3**, as the AIM charges seem to suggest, then the $\Delta H_{TS}$ values for these substrates should be on or near the line defined by **4**–**6** rather than well above it. That is because high barriers are considered in the PNS to arise from incomplete delocalization of transferred charge in the transition structure, which deprives the transition structure of at least part of the resonance stabilization enjoyed by the conjugate base product. If delocalization of charge is synchronous with its transfer from the base, there is no apparent reason for barriers much higher than those for **4**–**6**, once the effect of acidity is allowed for. We can adduce no alternative explanation for the high barriers.

The AIM charges are obviously measuring different effects than those measured by the NPA and Mulliken charges. None of the three measures of charge can be regarded as uniquely rigorous, for atomic charge is not a physical observable. It is thus worthwhile to inquire whether there is a plausible reason for the qualitative difference between the AIM and the other two measures of charge that would be compatible with the PNS and the computational evidence[1,2] and experimental evidence in solution[3–7] that support it. In order to explore this point, brief consideration of the way in which charge is allocated among the atoms by the AIM procedure is required.

In the procedure, a bond critical point along the bond path between two atoms is chosen so as to mark the region of minimum electron density between the atoms, and a surface cutting through the bond path at this point divides the electron density between the atoms. When all atoms attached to a given atom are taken into account, a "basin" containing that part of the molecular electron density attributable to that atom is created. The position of the bond critical point between any two atoms is expected to be determined by the $\sigma$ electron distribution.[55] This is qualitatively plausible because the $\sigma$ falls off more rapidly than the $\pi$ electron density with distance from the nucleus. The $\sigma$ electron distribution will consequently determine how *both* the $\sigma$ and $\pi$ electron densities are divided between the two atoms of a bond. The $\pi$ electron shifts of interest could thus easily be masked by opposing $\sigma$ electron shifts, a point we tried unsuccessfully to investigate (vide supra).[52–54]

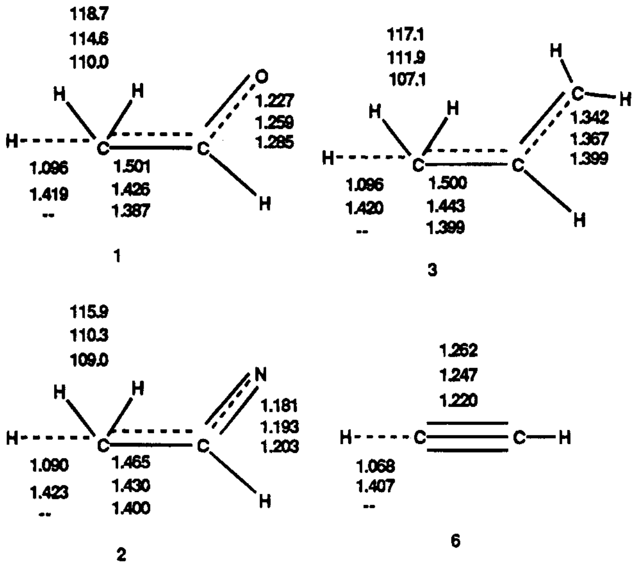

**Figure 3.** Bond lengths and angles (MP2/6-31+G*) for the carbon acid to conjugate base proton transfer. The number closest to the bond is the value for the reactant acid, the middle number is the value for the TS, and the outermost number is the value for the conjugate base product. The numbers above the two H's in **1**–**3** are the HCH bond angles.

In addition, a significant difference between the AIM on the one hand and the NPA or Mulliken charges on the other is that the electron distribution attributed to an atom by the AIM method is not usually centered on the nucleus[56] but it always is for the latter two methods. The experimental evidence for the PNS is based on linear free energy relationships which in turn are based on substituent effects on rates or equilibria where the substituent is either attached directly to the atom in question or at a fixed distance from it. Consequently the NPA and Mulliken charges with their fixed centers of electron distribution are likely to be better suited than the AIM charges for comparison with these experimental measures of charge.

One would expect the geometric parameters of the reactant, transition structure, and product to correlate with the electronic changes occurring in the course of the reaction. Figure 3 reports key geometric parameters for **1**–**3**, and for **6** to provide a comparison with an acid yielding a localized anion. In all cases the bond lengths and angles of the transition structures are between those of reactants and products, but the change is sometimes less and sometimes more than half complete. If the transition structure could be treated as a simple hybrid of reactant and product, all geometric parameters should be halfway between reactant and product for an identity reaction. In none of the transition structures **1**–**3** are all geometric parameters advanced to the same extent relative to the reactant-to-product change. In a general sense the behavior of the geometric parameters thus demonstrates imbalance. There is not, however, a correlation with the sorts of bond order changes a simple analysis based on the PNS would predict. This is not surprising, for the geometric parameters reflect changes

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in at least two other factors besides bond order: extent of rehybridization, and change in electron density. Note the lengthening of the CC bond of acetylene, which undergoes no change in formal bond order during the reaction but where electron density is increasing along the reaction path. In the case of **1** the increase in electron density at the α-carbon might be expected to *shorten* the CC bond because of increased attraction for the partial positive charge on the carbonyl carbon.

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**Supplementary Material Available:** Tables S1–S4 containing electronic energies in hartrees, zero point and vibrational energies, and complete listings at all levels of the enthalpy values derived from them (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal and can be ordered from the ACS; see any current masthead page for ordering information.

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