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Ab Initio Investigation of the Acetaldehyde-to-Acetaldehyde Enolate Proton Transfer

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Abstract: The energy profile for the carbon-to-carbon proton transfer from acetaldehyde to acetaldehyde enolate has been studied by semiempirical and ab initio methods. The ion–dipole complex is about 13 kcal/mol^{-1} below the separated reactants. It has what is best described as a head-to-tail (enolate oxygen to α-carbon of acetaldehyde) orientation, though the relative positions of the two components of the complex are strongly dependent on level. The barrier height (transition structure complex) is low by AM1 (5.7 kcal mol^{-1}) and PM3 (1.4 kcal mol^{-1}) but is substantial at all ab initio levels. The barriers at 3-21G to 6-31+G* Hartree–Fock levels run 21–25 kcal mol^{-1}, but Møller–Plesset corrections lower the 6-31+G* barrier considerably to 13–14 kcal mol^{-1} at MP2. The barrier rises to 15 kcal mol^{-1} at MP4SDTQ/6-31+G**//MP2/6-31+G*, the highest level examined. There are two almost equally energetic transition structures: trans-anti and cis-gauche.

Introduction

Most discussions of proton transfers have divided organic acids into two broad categories: "normal" or Eigen acids and carbon acids. The former encompass acids in which the proton is bound to an electronegative atom such as oxygen or nitrogen and which deprotonate at a diffusion-controlled (or close to diffusion controlled) rate when the deprotonation is exoergic.[1] Slower deprotonation results when the reaction is endoergic, but the only barrier is the endoergicity. Carbon acids, on the other hand, often deprotonate at dramatically slower rates than Eigen acids of comparable acidity.

It is desirable to subdivide carbon acids into at least two categories: those which deprotonate to give localized anions and those which deprotonate to give delocalized anions. The latter are of major importance in synthetic organic chemistry, for they are the precursors of enolates and other carbanions widely used as building blocks. These acids are also the most likely to deprotonate slowly and have been the subject of many mechanistic studies. The commonly accepted explanation for slow deprotonation has been that charge delocalization and heavy-atom reorganization must accompany the proton transfer, and the need for these extra processes raises the barrier to the overall reaction.[2,3]

More precisely, the extent of charge delocalization is believed to lag behind the extent of proton transfer in the transition state. This assumption provides an explanation for the otherwise puzzling observation that the rate of deprotonation of nitroalkanes is decreased by alkyl substitution but the equilibrium acidity is increased. Alkyl substitution destabilizes the negative charge on carbon in the transition state but stabilizes the carbon–nitrogen multiple bond in the product.[2] Evidence from substituted arylnitroalkanes supports this explanation.[4–6]

Recently Bernasconi[7–9] proposed a more general treatment, which he calls the principle of nonperfect synchronization (PNS). He presents reasons why charge delocalization should lag behind charge transfer from the base and argues that the resulting lag in development of resonance stabilization is responsible for an intrinsic barrier to the proton transfer. He has devised methods for obtaining the intrinsic barrier (the barrier when $\Delta G^\circ = 0$) and then dissecting it into contributions from charge delocalization, hydrogen bonding, solvation, and polarizability. The lag in charge delocalization, for example, is proportional to the difference between the Brønsted β for variations in the base and the Brønsted α for variations in the proton donor (such as an arylnitroalkane). Progress has also been reported in estimating the contribution of solvation to the intrinsic barrier.[9,10]

Separating solvent effects from other factors influencing reactions carried out in solution is at best a difficult and uncertain process. A more reliable approach is to eliminate the solvent effect by working in the gas phase. Flowing afterglow and ICR techniques have been used to study a considerable number of gas-phase proton transfers from organic acids.[11–16] Such studies have provided many valuable insights, but they require complex and expensive equipment. A further problem is that deducing reaction profiles from the experimental results is not always straightforward. A recent examination of alcohol-to-alkoxide proton transfers, for example, suggests barriers much higher than behavior in solution and high-level ab initio calculations would lead one to expect.[16]

Ab initio calculations provide an attractive alternative to experiment in cases where the experimental results are difficult to interpret. Recent experience has shown that they can give results of experimental accuracy provided they can be carried to a high enough level. The G2 method[17] is reported to give excellent agreement with experiment on the gas-phase acidities of a number of acids.[18] While this method would be too time-consuming to

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be practical for the present project, recent work at Rochester has found that MP2/6-31+G*//6-31+G* gives gas-phase acidities of carbon acids that are nearly always within 2–3 kcal/mol^{-1} of experiment.[19]

Published results on proton transfers from carbon acids that yield delocalized anions are sparse and inconsistent. Calculations on identity reaction proton transfers,

$$AH + A^- = A^- + HA$$

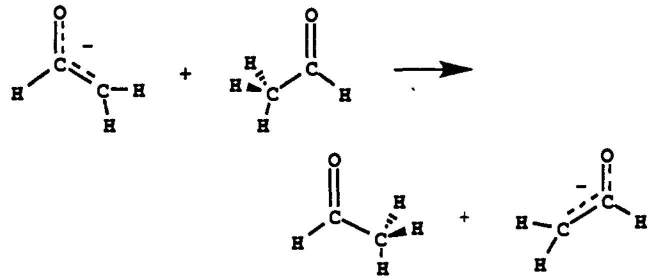
have been reported by Scheiner and co-workers for carbon acids that yield localized anions.[20–22] They report barriers of 5–23 kcal mol^{-1} which tend to be higher the weaker the acid. The reaction of hydroxide ion with propene is reported to have a barrier of 4 kcal mol^{-1} at the 4-31G level.[23] The deprotonation of acetaldehyde with amide, hydroxide, and fluoride ions, calculated at 6-31+G, is reported to show no barriers.[24] Reactions with the first two bases are exothermic, but even the endothermic reaction with fluoride showed no barrier beyond the endothermicity. During the course of the present work, I learned of unpublished results[25,26] in which substantial barriers were found for deprotonation of several carbon acids yielding delocalized anions. The reaction of acetonitrile with its conjugate base is reported to show a barrier of 9.7 kcal mol^{-1} at 4-31G.[27] A systematic study of a range of carbon acids yielding both delocalized and localized anions is clearly needed. Only if all the reactions are studied at the same ab initio level can valid conclusions be drawn about relative magnitudes of barriers and the factors contributing to these barriers. The present paper reports the beginning of such a study.

Computational Methods

The semiempirical calculations utilized Mopac version 6.0,[28] specifically, the AM1[29] and PM3[30] methods. The ab initio calculations utilized Gaussian 92.[31] Standard basis sets were used in all calculations: 3-21G,[32] 6-31+G,[33,34] 6-31+G*,[33,35] and 6-31+G**.[33,34] Correlation corrections were applied by the Møller–Plesset method.[36–40] The ΔH and ΔH^* values 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.[41,42] For species optimized at MP2/6-31+G*, ZPE values were scaled to 0.95. The enthalpy values were further corrected to 298 K for the contributions of the translational, rotational, and vibrational partition functions.[43] These corrections are printed in the Gaussian output from vibrational frequency calculations. The vibrational contribution is important only for low-lying frequencies (<500 cm^{-1}), of which a number are found in the ion–dipole complexes and transition structures of the present work. This correction is *not* based on scaled frequencies, because inspection of numerous frequency calculations makes it doubtful that low-lying calculated frequencies bear a predictable relation to the corresponding experimental frequencies.[44] Any error due to the failure to adjust these frequencies is likely to be small. That stationary points had been located was confirmed by frequency and force calculations that gave either no negative eigenvalues (for minima) or one negative eigenvalue (for transition structures).

Results and Discussion

The reaction studied was the proton transfer from the α-carbon of acetaldehyde to the α-carbon of acetaldehyde enolate:



The advantages of an identity reaction are that it removes any thermodynamic contribution to the barrier and that it is easier to locate the transition structure during the calculations. The procedure was to pick a graded range of basis sets of increasing complexity in the hope that the energies of the ion–dipole complex and the transition structure relative to the separated reactants would converge. Success in calculating gas-phase acidities at MP2/6-31+G*//6-31+G* (vide supra)[19] gave reason for hope that the desired convergence would occur at a practicable level.

Table 1 reports the energies in hartrees and Table 2 the zero-point energies in kcal mol^{-1} of the various species examined. Table 3 reports the enthalpy differences between reactants and ion–dipole complex (ΔH_{well}), ion–dipole complex and transition structure (ΔH^*), and reactants and transition structure (ΔH_{TS}). Table 4 lists the imaginary frequencies of the transition structures. Figure 1 shows the structures of the ion–dipole complexes at the various levels and the two stereoisomeric transition structures at 6-31+G*//6-31+G* (differences in the transition structures at different levels were too small to be visible in these drawings). Figure 2 shows NPA (natural population analysis[45,46]) charges and Figure 3 bond lengths for the reactants, ion–dipole complex, and transition structure at 6-31+G*.

The well depths in Table 3 clearly settle down to values near −13 kcal mol^{-1} at the highest levels and are reasonably well predicted even by the semiempirical methods. The correlation corrections make little difference, as does optimization at MP2/6-31+G* vs a single-point MP2 correction at the HF/6-31+G*

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Table 1. Energies of Stationary Points in the Acetaldehyde-to-Acetaldehyde Enolate Proton Transfer

level	E(reactants)[a]	E(complex)[a]	E(TS)[a] trans-anti	E(TS)[a] cis-gauche
AM1	−78.765[b]	−89.543[b]	−83.838[b]	−83.860[b]
PM3	−84.131[b]	−98.517[b]	−97.110[b]	−97.119[b]
3-21G//3-21G	−303.477 197	−303.509 748	−303.470 678	−303.470 660
6-31+G//6-31+G	−305.097 184	−305.122 753	−305.074 847	
6-31+G*//6-31+G*	−305.232 771	−305.252 982	−305.206 731	−305.206 793
MP2/6-31+G*//6-31+G*	−306.118 422	−306.139 927	−306.113 532	−306.113 723
MP3/6-31+G*//6-31+G*	−306.139 721	−306.161 743	−306.129 009	−306.129 224
MP4SDTQ[c]/6-31+G*//6-31+G*	−306.195 446	−306.217 235	−306.188 347	−306.188 5123
MP2/6-31+G*//MP2/6-31+G*	−306.122 746	−306.146 190	−306.118 707	
MP3/6-31+G*//MP2/6-31+G*	−306.141 704	−306.165 385	−306.130 798	
MP4SDTQ[c]/6-31+G*//MP2/6-31+G*	−306.201 974	−306.224 854	−306.194 493	
MP2/6-31+G**//MP2/6-31+G*	−306.178 894	−306.202 435	−306.176 204	
MP4SDTQ[c]/6-31+G**//MP2/6-31+G*	−306.261 200	−306.284 083	−306.255 009	

[a] In hartrees except as otherwise needed. [b] ΔH_f in kcal mol^{-1}. [c] Frozen core approximation.

Table 2. Zero-Point and Vibrational Energies in the Acetaldehyde-to-Acetaldehyde Enolate Proton Transfer[a]

quantity	6-31+G*	MP2/6-31+G*
ZPE(reactants)	65.909	62.056
ZPE(complex)	66.729	63.383
ZPE(anti-trans TS)	63.736	60.679
ZPE(cis-gauche TS)	63.792	*b*
VibE(reactants)	66.840	63.204
VibE(complex)	70.722	67.142
VibE(anti-trans TS)	66.686	63.715
VibE(cis-gauche TS)	66.728	*b*

[a] In kcal mol^{-1}. [b] Not calculated.

Table 3. Relative Enthalpies (in kcal mol^{-1}) of Stationary Points in the Acetaldehyde–Acetaldehyde Enolate Carbon-to-Carbon Proton Transfer[a]

level	ΔH_{well}	$\Delta H^{\ddagger}$	ΔH_{TS}[c]
Trans-Anti TS			
AM1 opt	−10.78	5.70	−5.08
PM3 opt	−14.39	1.41	−12.98
3-21G opt	−19.00	20.79	1.79
6-31+G opt	−14.61	26.33	11.72
6-31+G* opt	−11.25	25.28	14.03
MP2/6-31+G*//6-31+G*	−12.06	12.82	0.76
MP3/6-31+G*//6-31+G*	−12.39	16.80	4.41
MP4/6-31+G*//6-31+G* [b]	−12.24	14.39	2.15
MP2/6-31+G* opt	−13.21	13.96	0.75
MP3/6-31+G*//MP2/6-31+G*	−13.36	18.41	5.05
MP4/6-31+G*//MP2/6-31+G* [b]	−12.85	15.76	2.90
MP2/6-31+G**//MP2/6-31+G*	−13.27	13.17	−0.10
MP4/6-31+G**//MP2/6-31+G* [b]	−12.86	14.95	2.10
Cis-Gauche TS			
AM1 opt	−10.78	5.68	−5.10
PM3 opt	−14.39	1.40	−12.99
3-21G opt	−19.00	20.83	1.83
6-31+G* opt	−11.25	25.28	14.03
MP2/6-31+G*//6-31+G*	−12.06	12.74	0.68
MP3/6-31+G*//6-31+G*	−12.39	16.71	4.32
MP4/6-31+G*//6-31+G* [b]	−12.24	14.28	2.04

[a] Separated reactants taken as zero. Values are corrected to 298 K and for ZPE except for AM1 and PM3. See Computational Methods for details. [b] Frozen core approximation, MP4STDQ. [c] H(TS) − H(reactants).

Table 4. Reaction Coordinate Frequencies (in cm^{-1}) of Species in Acetaldehyde-to-Acetaldehyde Enolate Proton Transfer

quantity[a]	AM1	PM3	3-21G	6-31+G*	MP2/6-31+G*
$\nu^{\ddagger}_{L}$(t-a)	701i	748i	1508i	1855i	1312i
$\nu^{\ddagger}_{L}$(c-g)	700i	750i	1512i	1861i	*b*

[a] Abbreviations: t-a, trans-anti TS; c-g, cis-gauche TS. [b] Not calculated at this level.

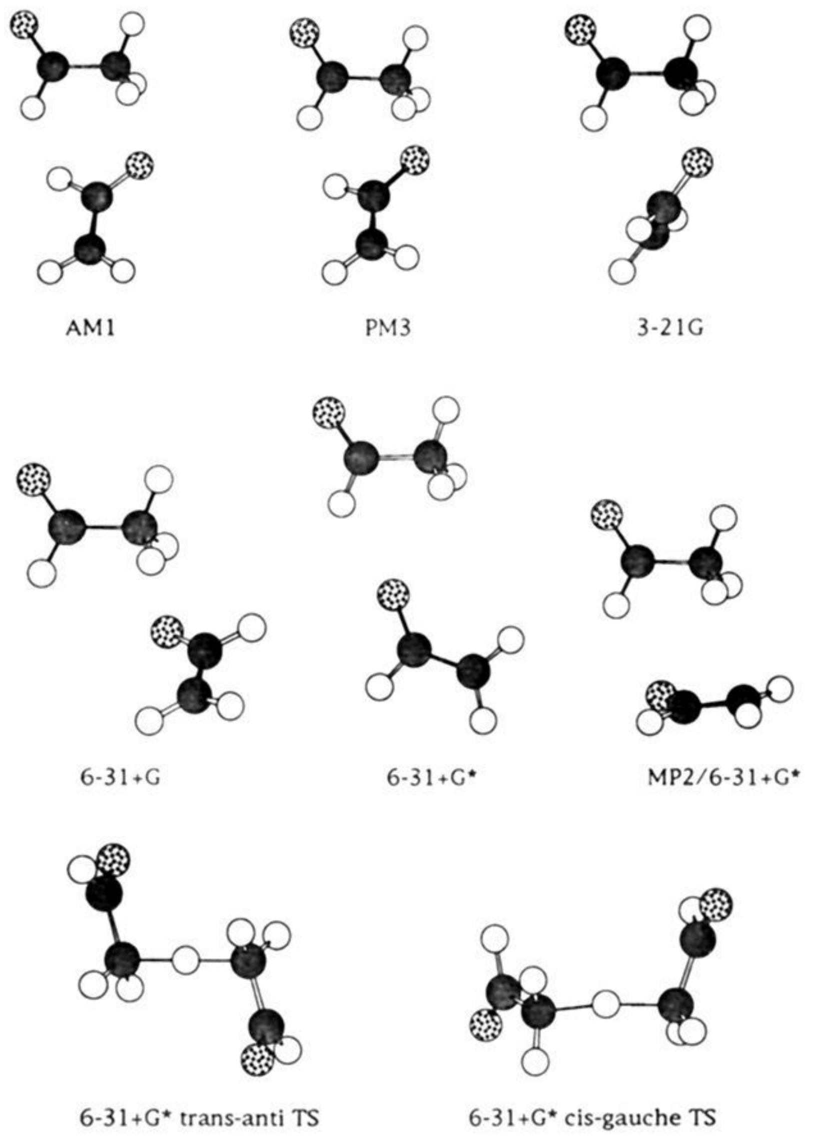

Figure 1. Ion–dipole complexes and the transition structures in the reaction of acetaldehyde and acetaldehyde enolate.

geometry. The only seriously deviant value is at 3-21G, and this is undoubtedly due to basis set superposition errors (BSSE). No attempt to correct for BSSE was made on the strength of recent reports that corrections are not quantitatively reliable and that computer time is better spent at higher levels, where such errors should be less significant.[47–49] That the well is not deeper is probably ascribable to the delocalized nature of the enolate, which should reduce the attraction the dipolar aldehyde feels for it.

The structures of the individual components of the ion–dipole complex differ little from the corresponding structures of the separated reactants. The NPA charges (Figure 2) and the bond lengths (Figure 3) are quoted only for the 6-31+G* optimized structures but are very similar at all of the ab initio levels. The relative positions of the components of the complex, however, depend strongly on the level (Figure 1). At most levels, the enolate oxygen is much closer than the enolate α-carbon to the

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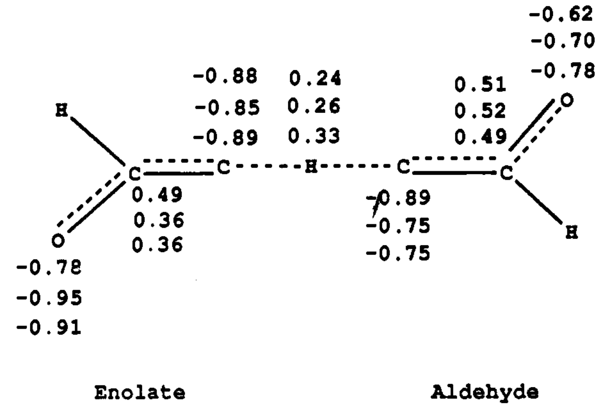

Figure 2. NPA charges (6-31+G*) in the acetaldehyde-to-acetaldehyde enolate proton transfer. The number closest to the atom is the charge in the TS, next in the complex, and next in the separated reactants.

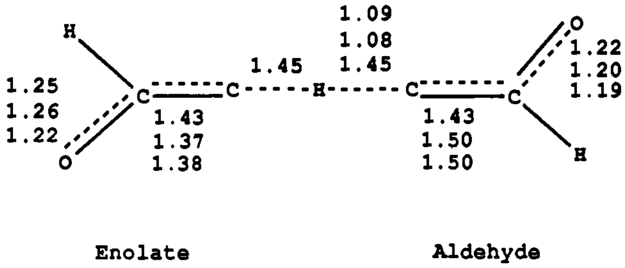

Figure 3. Bond lengths (6-31+G*) for the acetaldehyde-to-acetaldehyde enolate proton transfer. The bond length closest to the bond is that in the TS, next in the complex, and next in the separate reactants. Bond lengths are in angstroms.

α-hydrogens of the aldehyde (a head-to-tail orientation). The difference becomes smaller at the 6-31+G*//6-31+G* level, and the enolate α-carbon is almost as close as the enolate oxygen in the MP2/6-31+G*//MP2/6-31+G* complex. Although the enolate carbon must take up a position close to the aldehyde α-hydrogens during the ascent toward the transition state, only at the semiempirical levels could a stable tail-to-tail complex be found, and it was 1–2 kcal mol^{-1} above the head-to-head complex.

There is much greater variation in the barrier heights than in the well depths with level of calculation. The semiempirical methods, especially PM3, give very low barriers compared to the ab initio methods. The highest barriers result at the Hartree–Fock levels, reaching values of 25–26 kcal mol^{-1} at 6-31+G//6-31+G and 6-31+G*//6-31+G*. The correlation corrections at MP2/6-31+G*//6-31+G* and MP2/6-31+G*//MP2/6-31+G* approximately halve these values. Obviously, correlation corrections are much more important for the transition structure than for the complex. The barrier height increases from 13–14 at the MP2 levels to 17–19 at MP3 and back down to 15–16 kcal mol^{-1} at MP4SDTQ. The gas-phase acidity of acetaldehyde is closely predicted at this level: 367.0 vs experimental values of 365.8 ± 2.9 and 367.0 ± 2.0 kcal mol^{-1}.[50] A final effort at MP4SDTQ/6-31+G**//MP2/6-31+G* gives a barrier, 14.95 kcal mol^{-1}, that is only a little higher than those at the MP2 levels. It is clear that further elaboration of the basis set is likely to leave the barrier in a range of about 14 ± 1 kcal mol^{-1}. The behavior of this reaction in the gas phase is thus qualitatively as expected from slow solution-phase deprotonation at the α-positions of carbonyl compounds.

Geometry optimization at the MP2/6-31+G* level proved to be quite demanding of computer time, at least an order of magnitude greater than 6-31+G* with a single-point MP2 correction. The extra effort made little difference in the relative energies of the various species, but it did provide several useful insights. The substantially different structure of the ion–dipole complex has already been mentioned. The other is shown in Table 4, where it can be seen that optimization at MP2/6-31+G* lowers the reaction coordinate frequency to 1312i compared to the 1865i found at 6-31+G*. To the extent that the Bell theory of tunneling[51] is a reasonable picture of physical reality, this frequency provides a connection with experiment. Absolute values much above 1000i correspond to very large tunnel corrections and correspondingly large isotope effects for hydrogen transfer.[52] Since such large isotope effects are rare, the calculated frequency at MP2/6-31+G* is very probably more realistic than that at 6-31+G*. Scaling the frequencies would not affect this conclusion.

Bond lengths and bond angles of the transition structures vary little from one level to another. The length of the bond to the proton undergoing transfer, for example, is 1.40 Å in the semiempirical, 1.44–1.45 Å in the Hartree–Fock, and 1.42 Å in the MP2/6-31+G* optimized structures.

Of particular interest is the existence of two stereoisomeric transition structures of almost identical energies (within ca. 0.1 kcal mol^{-1}), the trans-anti and cis-gauche structures (Figure 1). (The trans and cis arrangements are defined by whether the oxygens are on the opposite (trans) or on 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.) The charge distributions and bond lengths are also the same (to the second decimal place) for both structures. It should be noted that the two isomers, though very close in energy, require for interconversion not only a conformational change about C···H···C but also 180° rotation about a carbon–carbon bond which has partial double bond character. There should thus be a substantial barrier to interconversion.

Although the present results find the cis-gauche and trans-anti structures to be of almost the same energy, Bernasconi and Wenzel[26] report that the trans-anti transition structure is about 10 kcal mol^{-1} above the cis-gauche. Comparison of the two sets of results show that the cis-gauche transition structures are essentially the same in both, but the trans-anti transition structure found in the present work has both α-carbon atoms pyramidal, while in the Bernasconi and Wenzel transition structure they are planar. The resulting improvement in bonding between the carbon atoms is evidently more than offset by less efficient bonding to the proton in transit.

No experimental data on the acetaldehyde + acetaldehyde enolate reaction could be found in the literature, but the acetone-d_6 + acetone enolate reaction studied by Brauman and Farneth[14] should be similar. They report a rate which is roughly 0.2% of the anticipated collision rate. They do not deduce a well depth or barrier height for this reaction, but they do apply quantum Rice–Ramsperger–Kassel theory to estimate that the barrier to reaction (E_A) is about 8 kcal mol^{-1} lower than the barrier to return to reactants (E_R). The present results place the proton-transfer barrier at or a little above the level of the reactants. Whether the discrepancy is real depends upon the similarity between the reaction profiles for acetone and acetaldehyde, a point on which no evidence is currently available.

It is of interest to inquire whether these results shed any light on the proposition (vide supra) that delocalization lags behind charge transfer in deprotonation of acids that yield delocalized anions. Figure 2 shows that the NPA charge distribution in the enolate is such that somewhat more negative charge resides on

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the oxygen than on the α-carbon. The polarization changes noticeably in the ion–dipole complex, negative charge becoming more concentrated on the oxygens of the enolate and aldehyde portions. There is, however, less than 0.01 unit of negative charge transferred from the enolate to the aldehyde portion, so the species can hardly be regarded as a charge-transfer complex. In the transition structures, substantially more negative charge resides on the α-carbon than on the oxygen. This represents a reversal of the negative charge distribution in the enolate, which is the product of deprotonation of the aldehyde. The calculations thus do provide support for incomplete delocalization in the transition structure of charge that has been transferred from the base.

In summary, the calculations are qualitatively in agreement with the conclusion, based on experiments in solution, that proton transfers from carbon acids that yield delocalized anions are intrinsically slow. While solvent effects may play a role in the condensed phase, they are not the major reason for the slowness. Evidence is presented that the delocalization of transferred charge is incomplete in the transition structure. Other carbon acids that yield formally delocalized conjugate bases are being examined for comparison with the present results.

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