Ab Initio Study on the Keto−Enol Tautomerism of the α-Substituted Acetaldehydes $XH_2CCH{=}O$ (X = H, BH_2, CH_3, NH_2, OH, F, CN, NC, and Cl): Comparison with the Tautomerism in α-Substituted Acetaldimines and Acetyl Derivatives

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Ab initio molecular orbital calculations have been performed on the α-substituted acetaldehydes $XH_2CCH{=}O$ (X=H, BH_2, CH_3, NH_2, OH, F, CN, NC, and Cl) to investigate the substituent effects on the keto−enol tautomerisms. Structures for all stationary point (ketones, enols, and transition states) were optimized and characterized at the MP2(full)/6-31G* and MP2(full)/6-31G** levels of theory. Intrinsic reaction coordinates (IRC) calculations were performed in order to connect transition structures with the appropriate tautomeric pairs. Results from various levels of calculations all show that the keto forms are thermodynamically more stable than the enol forms. At the G2 level, the former tautomers are energetically favored over the latter forms by 2.9, 5.6, 7.8, 9.6, 9.7, 10.2, 10.4, 11.8, and 12.1 kcal/mol for X = BH_2, CN, NC, NH_2, CH_3, OH, Cl, H, and F, respectively. All substituents except F stabilize the enol form relative to its keto counterpart as shown by the reduction of the energy gaps between the former and the latter forms. At the same G2 level, the respective activation energies of enolizations relative to the keto form were found to be 42.2, 58.0, 60.8, 61.8, 62.4, 63.3, 63.8, 64.5, and 65.3 kcal/mol for X = BH_2, CN, NC, NH_2, Cl, OH, CH_3, H, and F. Except for X = F, the α-substituted aldehydes all lower the barrier to the tautomeric interconversions. The substituent effects on the energetics in this study were compared with the results obtained from our previous theoretical investigations on the tautomeric interconversion of CH_3COX and XCH_2CHNH where X = BH_2, CH_3, NH_2, OH, F, CN, H, and Cl.

Introduction

Processes involving proton transfer between interconversion tautomers are of fundamental importance in synthetic and mechanistic chemistry. These include the keto−enol,[1] imine-enamine,[2] oxime-nitroso,[3] hydrazo-azo,[4] and phenol−keto[5] isomerizations. Among these processes, the most common studied form of tautomerism is that between a carbonyl compound (keto form) and its enol form. Under most circumstance these two tautomers are in an equilibrium which lies predominantly to the keto side, i.e., keto ⇆ enol. Most keto forms are thermodynamically more stable than their enol counterparts by more than 10 kcal/mol. This results in the equilibrium constant K_E = [enol]/[keto] < 10^{-8}. As a result of very low concentration of short-lived enol forms, K_E could not be accurately evaluated until the recent development of new methods of detecting unstable enol tautomers.[6] However, there are known stable enols, e.g., those of acetylacetone and malonaldehyde,[6c] in which the hydrogen bonding enhances their stabilities relative to the keto forms. Monofunctional enols have been found to be reactive intermediates in numerous organic reactions, e.g., electrophilic substitution in carbonyl compounds, oxy-Cope, Conia, and Carroll rearrangements, retro-Diels−Alder reaction, etc. In many of these reactions, the enolization of the carbonyl compound is the rate-determining step. Therefore, a change in the reaction condition (e.g., substituent effect) can lower the activation energy for the enolization and lead to an increase in reaction rate and yield. Acetaldehyde and vinyl alcohol are the prototypes for the keto/enol tautomerism. Vinyl alcohol is a transient intermediate in the very low-pressure pyrolysis of cyclobutanol.[7] It has a half-life of 30 min, before undergoing a tautomeric rearrangement to acetaldehyde which, by experimental estimate of heat of formations, is 13.2 kcal/mol more stable than vinyl alcohol. Ab initio molecular orbital calculations have been carried out on this tautomeric pair.[8] At the "G1" and MP4(fc)/6-311++G**//MP2(full)/6-31G* levels of theory, acetaldehyde is found to lie 11.2 and 13.35 kcal/mol below vinyl alcohol on the potential energy surface, respectively.

There have been studies on the tautomerism of the substituted acetaldehyde, particularly on the acetyl derivatives i.e., H_3C-(CO)X (X is the substituent). Recently we examined the substituent effects on the tautomerism of the acetyl derivatives[9] and α-substituted acetaldimines.[10] With the aim of investigating the similarity and difference of substituent effects resulting from the site (e.g., carbonyl carbon or α carbon) of substitution and functional group (e.g., carbonyl or imino), our continued interest in the substituent effects on the tautomeric interconversions has been extended to the α-substituted acetaldehydes. In this investigation, we employ high level ab initio molecular orbital calculations to examine the substituent effects in the tautomerism of $XH_2C(CO)H$, where X = H, BH_2, CH_3, NH_2, OH, F, Cl, CN, and NC.

The calculated activation energies of the 1,3-hydrogen shift and the relative stabilities of the substituted keto and enol forms in the tautomerism will be compared with our previous works on the α-substituted imine−enamine and the acetyl keto−enol tautomerisms.

Computational Methods

Ab initio molecular orbital calculations using second-order Moller−Plesset perturbation theories[11] with both 6-31G* and

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TABLE 1: Total Energies[a] (in hartrees) and Relative Energies (in kcal/mol, in parentheses) for the Keto and Enol forms, and Transition States (TS) for Their Interconversion

	MP2(full)/6-31G*			MP2(full)/6-31G**			G2		
X	keto	TS	enol	keto	TS	enol	keto	TS	enol
BH_2	−178.613 463 (0.0)	−178.539 423 (46.5)	−178.605 366 (5.1)	−178.656 477 (0.0)	−178.585 186 (44.7)	−178.651 732 (3.0)	−178.875 045 (0.0)	−178.807 809 (42.2)	−178.870 423 (2.9)
CN	−245.314 493 (0.0)	−245.212 270 (64.1)	−245.299 449 (9.4)	−245.340 955 (0.0)	−245.241 402 (62.5)	−245.329 608 (7.1)	−245.632 770 (0.0)	−245.540 414 (58.0)	−245.623 911 (5.6)
NC	−245.271 283 (0.0)	−245.164 490 (67.0)	−245.252 525 (11.8)	−245.297 837 (0.0)	−245.193 852 (65.3)	−245.282 885 (9.4)	−245.598 489 (0.0)	−245.501 541 (60.8)	−245.586 124 (7.8)
CH_3	−192.441 951 (0.0)	−192.328 663 (71.1)	−192.418 794 (14.5)	−192.495 628 (0.0)	−192.385 069 (69.4)	−192.475 954 (12.3)	−192.719 783 (0.0)	−192.618 129 (63.8)	−192.704 392 (9.7)
NH_2	−208.465 957 (0.0)	−208.355 645 (69.2)	−208.442 463 (14.7)	−208.513 793 (0.0)	−208.405 999 (67.6)	−208.494 048 (12.4)	−208.766 894 (0.0)	−208.668 416 (61.8)	−208.751 585 (9.6)
OH	−228.317 809 (0.0)	−228.205 320 (70.6)	−228.293 314 (15.4)	−228.356 801 (0.0)	−228.246 992 (68.9)	−228.336 033 (13.0)	−228.646 467 (0.0)	−228.545 655 (63.3)	−228.630 291 (10.2)
Cl	−612.343 706 (0.0)	−612.232 477 (69.8)	−612.319 507 (15.2)	−612.370 131 (0.0)	−612.261 843 (68.0)	−612.349 654 (12.8)	−612.676 104 (0.0)	−612.576 706 (62.4)	−612.659 499 (10.4)
H	−153.301 992 (0.0)	−153.186 124 (72.7)	−153.274 756 (17.1)	−153.337 300 (0.0)	−153.224 668 (70.7)	−153.313 800 (14.7)	−153.523 336 (0.0)	−153.420 541 (64.5)	−153.504 487 (11.8)
F	−252.318 407 (0.0)	−252.201 563 (73.3)	−252.291 499 (16.9)	−252.345 107 (0.0)	−252.231 352 (71.4)	−252.321 839 (14.6)	−252.675 937 (0.0)	−252.571 956 (65.2)	−252.656 725 (12.1)

[a] ZPVE included. Scaling factor: 0.9427.

6-31G**[12] basis set were performed for all geometry optimizations with the Gaussian 92[13] and Gaussian 94[14] series of programs. To better describe the hydrogen shift in the tautomeric processes MP2 (full)/6-31G** geometry optimizations were also carried out. Harmonic vibrational frequencies were computed at the same level of theory as the geometry optimization in order to characterize the stationary points as local minima (equilibrium structure) or first-order saddle points (transition structures) on the potential energy surface (PES) and to evaluate the zero-point vibration energy (ZPVE). Since the calculated harmonic vibrational frequencies overestimate the experimental values, the former was corrected by the scaling factor of 0.9427.[15] To further correct for electron correlation, single-point calculations were completed at the G2 level of theory for the stationary points. To establish the connection between the transition structures and the corresponding equilibrium structures, the reaction pathways were followed using the intrinsic reaction coordinate (IRC)[16] procedure. The natural bond orbital (NBO)[17] technique was applied to calculated the bond order and natural population in order to analyze the intramolecular bondings and interactions.

Results and Discussion

We will first present and discuss the results obtained in the current study on the α-substituted acetaldehydes which will then be compared with our previously reported analogous works on the acetyl derivatives and α-substituted acetaldimines. Unless specifically noted otherwise only the results based on the G2 will be used in discussing the energetics (section I) for the α-substituted acetaldehydes. For uniformity the three tautomerisms will be compared with the results from the MP2(full)/6-31G* calculations (section II).

(I) Energetics. A summary of the calculated total energies, zero-point vibrational energies (ZPVE), relative energies (keto vs enol form), activation energies for enolizations and ketonizations at the MP2(full)/6-31G*//MP2(full)/6-31G*, MP2(full)/6-31G**//MP2(full)/6-31G**, and G2 levels of theory are compiled in Table 1.

(a) Relative Energies of the Keto and Enol Forms. As seen in Table 1, for each tautomerism considered here, the keto form is thermodynamically more stable than the enol form at all levels of calculations. The relative energies range from 2.9 kcal/mol for X = BH_2 to 12.1 kcal/mol for X = F, with the relative energy decreasing in sequence BH_2 < CN < NC < NH_2 < CH_3 < OH < Cl < H < F. The inclusion of electron correlation lowers the relative energies (in comparison with those of the HF/6-31G** results) by an average of 0.6 and 2.7 kcal/mol at the MP2(full)/6-31G**//MP2(full)/6-31G** and G2 levels of theory, respectively. Table 1 shows that all enol forms, except when X = F, increase their stability relative to the keto forms with the stability increasing in sequence F < Cl < OH < CH_3 < NH_2 < NC < CN < BH_2.

The remarkable substituent effect on the increasing stabilities of the enol forms when X = BH_2, CN, and NC may be rationalized in terms of the stabilizing effect by delocalizing the π electron density of the C═C double bonds to these substituents. This is attributed to the π electron donations from the C═C bond to the vacant p orbital on boron for X = BH_2 and to the π^* orbital on the −CN and −NC when X = CN and NC leading to stabilization of the enol forms. An analysis of the results of natural bond orbital (NBO) calculations shows a notable correlation between the increase in stability of the enol forms (relative to the keto forms) and the stabilization energy (SE) is observed. It is found that the variation in the latter with the substituent correlates with the quantity of charge transfer (qct) from the donating NBO of the C═C bond to the accepting NBO in the empty p orbital of boron for X = BH_2 (0.146) or the π^* orbital for X = CN (0.062) and NC (0.034). The more the electron density is transferred, the more the enol form is stabilized. Of the rest of substituents considered in this study, those with lone-pair electrons on the electronegative atoms (X=NH_2, OH, F, and Cl) are π donors and σ acceptors while the CH_3 is usually π donating to the π^* of the C═C bond. The interaction between the lone-pair electrons of the former groups and π^* orbital of the C═C bond and the interaction between the π orbital of the CH_3 and π^* orbital of the C═C bond are all stabilizing in the enol forms. In contrast to the previously discussed series of X = BH_2, CN, and NC where the π conjugative effect (in terms of qct) is the dominating stabilizing factor, the present series of substituents demonstrate a predominantly inductive effect (shown as group electronegativity). The calculated results also show a good linear correlation between the relative energies and the group electronegativities of the isoelectronic series of substituents (X = CH_3, NH_2, OH, and

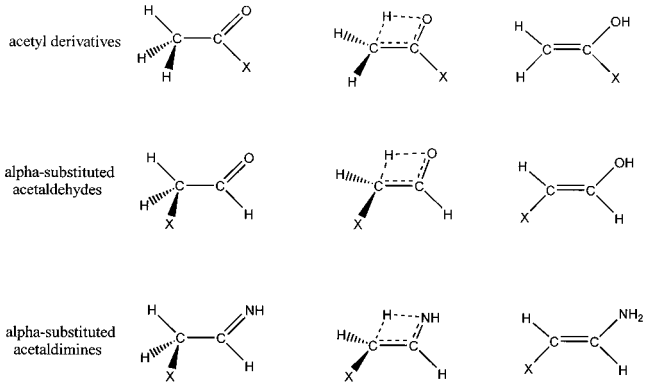

Figure 1. The tautomerization equilibria compared in this study (X = H, BH_2, CH_3, NH_2, OH, F, Cl, and CN).

F). Being the most electronegative species in the series, fluorine has the least tendency to release the lone-pair electron and hence is least stabilizing in the enol form among the substituents in this isoelectronic series. As a third period and less electronegative element, the lone-pair electrons of chlorine are more polarizable, and chlorine it is therefore more π donating and stabilizing than OH and F.

(b) Activation Energies. An examination of the data shown in Table 1 leads to the following observations: (1) The energy barriers to the enolizations are in the following order: BH_2 (42.2) < CN (58.0) < NC (60.8) < NH_2 (61.8) < Cl (62.4) < OH (63.3) < CH_3 (63.8) < H (64.5) < F (65.2) where the number in parentheses are the energy barriers in kcal/mol. It is seen from this sequence that the substituents, except where X = F, all in general and BH_2 in particular reduce the activation energy for enolization with respect to acetaldehyde (X = H). The same ordering is found from the MP2 (full)/6-31G** calculations with barriers ca. 5 kcal/mol higher than those obtained from G2 calculations. (2) The activation energy for the enol form to tautomerise increases in the order BH_2 (39.3) < Cl (52.0) < NH_2 (52.2) < CN (52.4) < H (52.7) < NC (53.1) = OH (53.1) < F (53.2) < CH_3 (54.1). It is clear that, with the exception of X = BH_2, the substituents have little effect on the ketonizations as the barriers to the interconversions differ from that of the parent molecule within 1.4 kcal/mol. A similar trend is found is found in the series obtained at the MP2 (full)/6-31G**//MP2 (full)/6-31G** level of theory, where the energy barriers vary from 41.7 kcal/mol for the substituent BH_2 to 57.1 kcal/mol for the CH_3 substituent.

(II) Comparison with the Imino and Acetyl Analogues. The above-discussed results for the current calculations of the α-substituted acetaldehydes are compared with the analogous tautomerisms we have previously reported for the acetyl derivatives and the α-substituted acetaldimines (Figure 1). It is seen that the former series are the positional isomers (with respect to the site of substituent) whereas the latter are the imino analogues of the α-substituted acetaldehydes.

(a) Comparison of Relative Stabilities of the Tautomers. The relative energies as determined with at MP2 (full)/6-31G* are given in Table 2 for all the tautomers and their transition structures. Figure 2 provides the graphical representations for the relative energies of the tautomeric pairs in the three series. It is seen that the lines of two α-substituted tautomeric series are virtually parallel with that of the acetaldehydes above the acetaldimines producing a nearly uniform gap of ca. 10 kcal/mol between them. In contrast, the line for the acetyl derivatives lies above the former lines and is quite different from them. The general trend found above indicates that (i) the functional

TABLE 2: Relative Energies (kcal/mol)[a]

	H_3CCXO			XCH_2CHO			XCH_2CHNH		
X	keto	TS	enol	keto	TS	enol	keto	TS	enol
BH_2	0.0	67.1	13.0	0.0	46.5	5.1	0.0	41.8	−5.7
CN	0.0	73.4	16.0	0.0	64.1	9.4	0.0	59.4	−1.2
Cl	0.0	79.7	29.0	0.0	69.8	15.2	0.0	66.1	5.6
F	0.0	83.0	33.6	0.0	73.3	16.9	0.0	68.2	6.6
OH	0.0	79.1	35.3	0.0	70.6	15.4	0.0	68.2	5.9
NH_2	0.0	70.7	31.7	0.0	69.2	14.7	0.0	66.2	5.6
CH_3	0.0	71.5	18.6	0.0	71.1	14.5	0.0	69.1	5.5
H	0.0	72.9	17.1	0.0	72.7	17.1	0.0	70.7	7.9

[a] Calculated at the MP2(full)6-31G*//MP2(full)/6-31G* level with ZPVE corrections.

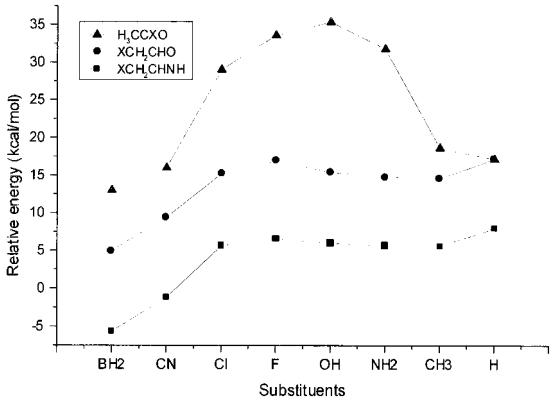

Figure 2. Relative energies of the tautomers.

group (NH_2) of enamines is a better π donor than that of the OH group in the enols. Therefore it stabilizes the α-substituted enamine relative to the imine more than that of the enol form to the keto form. In particular, for the substituents with empty π orbital (X = BH_2) or π^* orbital (X = CN) to accept the π electron density from the C═C double bond, the "pull and push" effect becomes operative leading to a further stabilization of the enamine and the enol form. Having the largest effect, the enamines are found to be more stable than the imines in both two substitutions. (ii) In all three tautomeric series, the π donating substituents (X = Cl, F, OH, and NH_2) increase the relative stability of the keto form and the imine, especially with the acetyl derivatives, where the substituents donate the π electron density directly to the adjacent carbonyl π^* orbital. This readily stabilizes the keto forms and leads to a significant increase in their stabilities relative to the enol form. (iii) XCH_2-CHNH and XCH_2CHO behave much more similarly than H_3-CCXO.

(b) Comparison of Activation Energies of the Tautomeric Interconversions. As can be seen by comparison of the appropriate columns, shown in Table 2 and illustrated in Figure 3, for each substituents the barriers to enolization are acetyl derivatives > α-substituted acetaldehydes > α-substituted acetaldimines. Being adjacent to the carbonyl group, the π donation from the substituents to the π^* orbital of the C═O bond on the acetyl derivatives is most stabilizing to the keto forms among the three tautomeric series in this study. This results in a substantial increase in the activation energies for enolizations in the acetyl series, which are in 67.3∼81.9 kcal/mol range with a variation of ca. 15 kcal/mol. The line presenting the α-substituted acetaldehydes with barriers varying from 46.6 to 73.5 kcal/mol lies ca. 8∼21 kcal/mol below the acetyl line and ca. 3∼5 kcal/mol above that of the α-substituted acetaldimines. The latter has the activation energies ranging from 41.8 to 70.7 kcal/mol with a variation of ca. 29 kcal/mol, about the same as that of the α-substituted acetaldehydes (∼27 kcal/

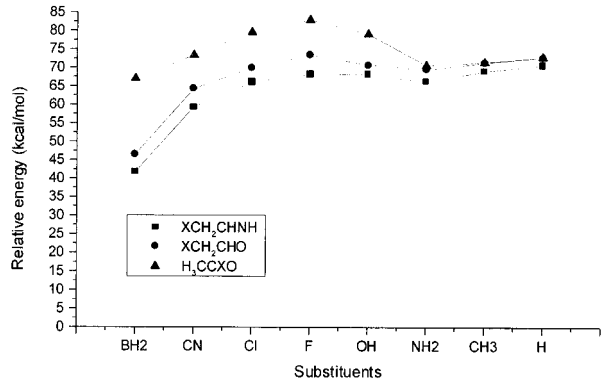

Figure 3. Activation energies for the enolizations.

mol). This indicates that their substituent effects are very similar. The same trend is also noted for the barriers to the ketonizations for the α-substituted series, as indicated by the linear regression calculations. In contrast, the barriers to the tautomeric interconversions for the acetyl derivatives correlate poorly with those of the two α-substituted series. For all substituents, except when $X = BH_2$ and CN, the order of the barrier to ketonization, α-substituted acetaldimines > α-substituted acetaldehydes > acetyl derivatives, is the reverse of that of enolization in the reaction profile.

On the whole, a similarity of the substituent effects on the features and trends in energetics is noted in the α-substituted keto/enol and imine/enamine series, while there is a difference between these two series and the acetyl derivatives.

Conclusions

In this work, we have carried out high level ab initio molecular orbital calculations up to the G2 to examine the effect of various substituents on the keto/enol tautomerism for nine α-substituted acetaldehydes. For uniformity, a comparison of the calculated results in this paper with those in our previous paper for the tautomeric interconversions in the acetyl derivatives and α-substituted acetaldimines is also reported at the MP2(full)/6-31G*//MP2(full)/6-31G* level of theory. The conclusions from this study are summarized as follows

At all level of calculations, the keto form is thermodynamically more stable than the enol form. The relative energies at the G2 level range from 2.9 kcal/mol for $X = BH_2$ to 12.1 kcal/mol for X = F, with the relative energy increasing in sequence $BH_2 < CN < NC < NH_2 < CH_3 < OH < Cl < H < F$. The inclusion of electron correlation lowers the relative energies (with respect to those of the HF/6-31G** results) by an average of 2.7 kcal/mol at the G2 level.

The energy barriers to enolizations are in the following order: BH_2 (42.2) < CN (58.0) < NC (60.8) < NH_2 (61.8) < Cl (62.4) < OH (63.3) < CH_3 (63.8) < H (64.5) <F (65.2) where the numbers in parentheses are energy barriers in kcal/mol at the G2 level, whereas the barriers to ketonizations are BH_2 (39.3) < Cl (52.0) < NH_2 (52.2) < CN (52.4) < H (52.7) < NC (53.1) = OH (53.1) < F (53.2) < CH_3 (54.1).

Similarities in the substituent effect on the relative energies of the tautomers and the activation energies of the enolizations and ketonizations also exist between the two α-substituted tautomeric series. These relative energies and activation energies are poorly correlated with the corresponding ones from the acetyl series.

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Supporting Information Available: Complete set of the optimal geometric parameters and preferred conformations in optimized structures for the ketones, transition states, and enols (MP2 (full)/6-31G**). Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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