

Enols and Enolates of Carboxylic Acid Derivatives. A G2(MP2) ab Initio Study

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The effect of substituents on the stability of enols and enolates relative to their oxo (C=O) forms is explored using the G2(MP2) ab initio method for CH₃COX (14 substituents). Calculated enthalpies of reaction for enolate formation agree well with experimental gas-phase data. Relative to acetaldehyde, enolate formation from a carbonyl compound is favored by the presence of both σ and π electron-withdrawing groups and disfavored by π -donating groups. Isodesmic reactions show that electron withdrawal stabilizes the enolate more than the oxo form. Donation from the π system stabilizes the oxo form but has little or no effect on the enolate form. Destabilization due to electrostatic repulsion between the oxygen bound carbon and the attached atom for X = {CF₃, CHO, C≡N} is more severe in the oxo than enolate form. The effect of substituents on the stability of both enolates, H₂CC(O⁻)X, and ethoxide derivatives, CH₃CH(O⁻)X, are shown to be very similar. Relative to acetaldehyde, the heats of reaction of CH₃COX for both enolate formation and hydride addition are also similar. For enols, both σ electron-withdrawing and π -donating substituents favor the oxo over the enol form. Isodesmic reactions show that substituents have a parallel effect on stability in the oxo and enol forms, as well as in ethene derivatives. The magnitude of these effects increases with the polarity of the double bond, i.e., carbonyls > enols > ethenes. To summarize substituent effects, enols can be thought of as ethene derivatives which are slightly polarized by the hydroxy group, while enolates can be thought of as ethoxide derivatives which are perturbed by the double bond.

Introduction

Enols and enolates are important reactive intermediates in both chemistry and biochemistry. In biochemistry, many biologically important elimination and racemization reactions are thought to proceed through enol and enolate intermediates.¹ The enolates of aldehydes and ketones as well as those of esters and amides have received a great deal of attention due to their use in carbon-carbon bond formation.² While the enols of aldehydes and ketones are ubiquitous and thoroughly investigated,³ those of carboxylic acid derivatives are quite elusive and consequently have received less study.⁴ Intrigued by the large divide in the amount known about enols versus enolates of esters and amides and as an aid in designing future experiments, I initiated a computational study on the effect of substituents on the formation of enols and enolates from carbonyl compounds.

In solution, the energy for converting carbonyl compounds to their enolates is widely available from the relevant pK_a data.⁵ These data are not without controversy, as evidenced by a recent article on the acidity of ethyl acetate in water.⁶ This latter study illustrates how the equilibrium between the oxo and enolate form, i.e., [CH₃COX + HO⁻ ⇌ H₂CC(O⁻)X + HOH], can be highly dependent on the solvent and on the counterion of the base. Thus, gas-phase data are necessary to understand the intrinsic effects of substituents on enolate formation. Such data for several CH₃COX derivatives exist.⁷ Yet, it is desirable to use ab initio methods to calculate carbonyl acidities for two reasons: (1) some gas-phase data do not exist or have large uncertainties and (2) a comparison between enols and enolates should employ similar methodology. There exist ab initio calculations for enolate reactivity, including carbon versus oxygen alkylation of a ketone enolate,⁸ protonation of the enolate of acetaldehyde,⁹ deprotonation of acetic acid,¹⁰ racemization of aspartic acid and asparagine,¹¹ and asymmetric

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protonation of a chiral ester enolate.¹² However, there is no recent work on the effects of substituents on enolate stability.

The enols of aldehydes and ketones are well characterized; the oxo-enol equilibrium constant³ and enol acidities^{3,13} are known for a variety of alkyl and aryl substituents. The persistent enols of diaryl esters and amides have recently received attention.^{4a-c} Several less stable carboxylic acid enols have been the focus of recent work by Kresge et al.^{4d-f} As with enolates, it is desirable to obtain gas-phase data to best study the intrinsic effects of substituents on enol formation. The threshold ionization energies obtained from generation of the radical cations of both enols and of carbonyl compounds have been used to determine oxo-enol equilibrium constants for aldehydes and ketones in the gas phase.¹⁴ No work of this fashion has been done on carboxylic acid derivatives, presumably due to the difficulty of generating the requisite enols.

Ab initio calculations suffer from no such limitations. There have been recent high quality calculations on the enols of aldehydes and ketones,¹⁵ on acidities of the enols of aldehydes and ketones,¹⁶ of vinyl alcohol,¹⁷ and of alkyl and silyl substituted aldehydes and ketones.¹⁸ The latest study on the enols of carboxylic acid derivatives was conducted by Heinrich, Koch, Frenking, and Schwarz (HKFS) over 10 years ago.¹⁹

Thus, I have undertaken a systematic high level computational study of the intrinsic factors which stabilize the enols and enolates of CH₃COX using the G2-(MP2) method. The G2 methodology and its time-saving variant, G2(MP2), has been shown to give proton affinities, dissociation energies, ionization energies, and electron affinities with an average absolute deviation from experimental values of 1.21 kcal/mol (G2) and 1.58 kcal/mol (G2(MP2)).²⁰ In a recent discussion on the effectiveness of various computational models, it was found that G2(MP2) is highly accurate, though computationally demanding.²¹ Importantly, Turecek and Cramer have used the G2(MP2) method to study alkyl-substituted enols.¹⁵

There are two major goals of this study. The first is to understand the effects on enol and enolate formation by three groupings of substituents: (1) the attached atom is varied {H, CH₃, NH₂, OH, F}, (2) the hybridization of the attached carbon is changed {CH₃, CHCH₂, C≡CH}, and (3) the attached atom is bound to electronegative

atoms {CF₃, NO₂, CHO, C≡N}. The last group can be further subdivided into the purely inductive {CF₃} versus those with large {CHO, NO₂} and moderate {C≡N} charge-transfer components.²² The second goal is to analyze the findings above in the context of studies of carbonyl compounds and their reactions. Specifically, substituent effects on enols will be shown to behave much like those on the C=C functionality, while substituent effects on enolates parallel those of the C-O⁻ functionality.

Computational Methods. Energies were calculated using the G2(MP2) procedure^{20a} using the Gaussian 94 program suite.²³ In short, geometries are optimized using the 6-31G* basis set²⁴ at the level of Moeller-Plesset second-order perturbation theory using all electrons (MP2=full).²⁵ All stationary points were confirmed with analytical second derivatives. Single point calculations at the QCISD(T)/6-31G**,²⁶ MP2/6-31G**, and MP2/6-311+G(3df,2p) levels are then performed to correct for correlation beyond the MP4 level and for basis set deficiencies. A zero point correction is added using 0.893 times the HF/6-31G*//HF/6-31G* determined vibrational frequencies. Finally, a higher level correction of -0.005 Hartrees per valence electron pair is added.

Results and Discussion

Enolates. 1. Substituent Effects on Enolate Formation. The energies for enolate formation from CH₃-COX to H₂C=C(O⁻)X are listed in Table 1 under the heading $\Delta H_{\text{enolate}}$ and are relative to X = H, or {H}, which is set to 0.0 kcal/mol. (Second row species such as H₂C=C(O⁻)Cl proved computationally unstable relative to the ion-dipole complex of H₂C=C=O and Cl⁻ and hence were not studied. This instability is presumably due to the increased stability of second row versus first row anions.) The absolute energy for deprotonation of acetaldehyde is calculated to be 366.2 kcal/mol which is extremely close to the gas-phase experimental value of 365.9 kcal/mol.⁷ Experimental gas-phase values of $\Delta H_{\text{enolate}}$ are given in parentheses beside the computational ones in Table 1. The agreement of the experimental and calculated data is very good, with an average deviation of 2.5 kcal/mol (7 data points, not {H}). The agreement would be significantly better if not for CH₃-CON(CH₃)₂, where the calculated and experimental values differ by 8.2 kcal/mol.

Two trends are apparent from Table 1. (Note that positive values of $\Delta H_{\text{enolate}}$ indicate that enolate formation is energetically unfavorable relative to acetaldehyde.) First, $\Delta H_{\text{enolate}}$ decreases with increasing electron-withdrawing ability of X as seen within each of three groupings: (1) variation of the electronegativity of the

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Table 1. Isodesmic Reactions of CH₃COX and Its Enol and Enolate^a (kcal/mol)

X	ΔH enolate ^b		enolates			ΔH CH ₃ COX	enols		
			ΔH H ₂ CC(O ⁻)X	ΔH CH ₃ CH(O ⁻)X	ΔH reduce		ΔH enol	ΔH H ₂ CC(OH)X	ΔH H ₂ CCHX
H ^c	0.0	(0.0)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃	2.6	(3.3)	7.9	10.0	0.4	10.5	1.6	8.8	4.0
NH ₂	10.4		19.4	22.1	7.8	29.8	14.1	15.7	10.4
N(CH ₃) ₂	9.8	(1.6)	10.6		20.3				
OH	4.3		28.6	32.2	0.7	32.9	16.5	16.4	11.8
OCH ₃	6.8	(6.0)	25.5			32.3	16.0	16.3	
F	-4.7	(-5.6)	31.6	39.0	-12.2	26.8	14.6	12.3	6.9
CH ₂ CH ₃	2.2	(4.3)	3.8	12.0	-5.9	6.0	0.6	5.4	
CHCH ₂	0.8	(-2.6)	7.1	7.8	0.1	7.9	-1.5	9.5	6.5
CCH	-9.6		12.7	7.9	-4.9	3.1	-2.0	5.1	3.2
CF ₃	-16.7 ^d		5.1 ^d	11.9	-23.5	-11.7	-1.7	-10.0	-8.8
CHO	-9.7		13.9	13.5	-9.3	4.2	-7.0	11.3	6.6
CN	-23.1	(-21.5)	22.5	25.1	-25.7	-0.6	-1.2	0.6	0.6
NO ₂	-23.5		23.6	e	e	0.2	-1.7	1.9	0.8

^a All energies use the G2(MP2) methodology and are relative to X = H, which is set to 0.0 kcal/mol. Symbols are defined in text. ^b Experimental gas-phase data given in parentheses and are from ref 7. ^c Absolute energies in Hartrees are -153.57297 for CH₃CHO, -153.55520 for H₂C=C(OH)H, -152.98936 for H₂C=C(O⁻)H, -154.15822 for CH₃CH₂O⁻, -78.41430 for H₂C=CH₂, and -40.40967 for CH₄. ^d Stationary points were calculated at the MP2/6-31G* geometry as the MP2=full/6-31G* geometry gave an imaginary vibrational frequency. ^e This anion was computationally unstable relative to the ion-dipole complex of NO₂⁻ and CH₃CHO.

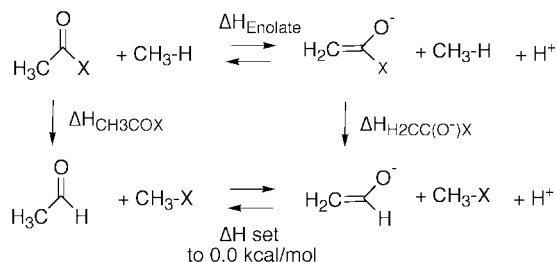
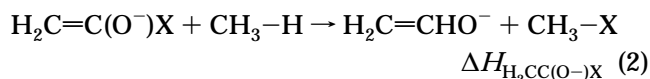
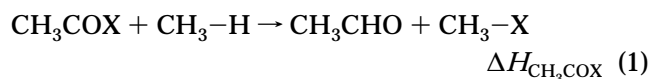


Figure 1. Thermodynamic cycle showing the connection between the isodesmic reactions, $\Delta H_{\text{H}_2\text{CC}(\text{O}^-)\text{X}}$ and $\Delta H_{\text{CH}_3\text{COX}}$, and the energy of enolate formation of CH₃COX, $\Delta H_{\text{enolate}}$, relative to that of CH₃CHO.

attached atom {NH₂ (10.4) > OH (4.30) > F (-4.7)}, (2) change of the hybridization of the attached carbon {CH₂-CH₃ (2.2) > CH=CH₂ (0.8) > C≡CH (-9.6)}, and (3) replacement of nonpolar C-H or C-C bonds of the attached carbon with polar bonds {CH₃ (2.6) > CF₃ (-16.7), CH=CH₂ (0.8) > CH=O (-9.7), C≡CH (-9.6) > C≡N (-23.1)}. Second, $\Delta H_{\text{enolate}}$'s for {H,CH₃} are intermediate between {F} and {NH₂,OH}. Apparently, the presence of basic lone pair(s) on X raises the value of $\Delta H_{\text{enolate}}$, and this effect overrides the lowering of $\Delta H_{\text{enolate}}$ due to electronegativity. Both trends can be understood using the thermodynamic cycle illustrated in Figure 1.

Written below are isodesmic reactions for both CH₃-COX (1) and H₂C=C(O⁻)X, (2), reactions used in Figure 1. It is worth keeping in mind that positive values of ΔH in reactions 1 and 2 denote that the X substituent stabilizes the examined functionality relative to CH₃X. Isodesmic reaction 1 describes the effects of substituents on CH₃COX and is listed in Table 1 under the heading $\Delta H_{\text{CH}_3\text{COX}}$. This reaction has been thoroughly analyzed by Wiberg et al.²⁷ Briefly, groups which are more electronegative than carbon and those which are π donating stabilize C=O, each effect of comparable importance. The partial negative charge of the electron-withdrawing group has a favorable electrostatic interaction with the partially positive carbon of the polarized C=O bond. Furthermore, as the substituent withdraws

more electron density, the carbonyl carbon becomes more positive and the electrostatic interaction is increased. Basic lone pairs lead to stability by delocalizing electron density into the π system of the C=O bond. It was also found that the strongly electron-withdrawing groups {CF₃, CHO, CN, NO₂} are less stabilizing than {CH₃}. This is due to electrostatic repulsion between the carbonyl carbon and the partially positive attached atom. Using energies calculated at the HF/6-31G**/HF/3-21G level of theory, HKFS arrived at similar conclusions over 10 years ago.¹⁹



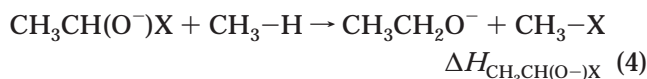
$$\Delta H_{\text{CH}_3\text{COX}} - \Delta H_{\text{H}_2\text{CC}(\text{O}^-)\text{X}} = \Delta H_{\text{enolate}} \quad (3)$$

Isodesmic reaction 2 describes the effects of substituents on H₂C=C(O⁻)X and is listed in Table 1 under the heading $\Delta H_{\text{H}_2\text{CC}(\text{O}^-)\text{X}}$. In general, the value of $\Delta H_{\text{H}_2\text{CC}(\text{O}^-)\text{X}}$ increases with the electron-withdrawing ability of X. For the groups {F > OH > NH₂ > CH₃}, this effect can be explained as increasing inductive stabilization of the negatively charged oxygen atom. Basic lone pairs appear to have no effect on $\Delta H_{\text{H}_2\text{CC}(\text{O}^-)\text{X}}$, unlike the sizable contribution made to $\Delta H_{\text{CH}_3\text{COX}}$. When the s character on the attached carbon increases in the series {CH₂CH₃, CHCH₂, CCH}, stabilization also increases, though the magnitude of this effect is small. Surprisingly, the powerfully electron-withdrawing substituents {CF₃, CHO, CN, NO₂} provide only modest stabilization; {CN, NO₂} are comparable to {NH₂, OH} while {CF₃, CHO} are less stabilizing than {CH₃}. Presumably, electrostatic repulsion between the partially positive oxygen bound carbon and the partially positive attached atom in {CF₃, CHO, CN, NO₂} offsets some of the inductive stabilization these groups provide. Since the oxygen bound carbon is more positive in the oxo than in the enolate form, the repulsion is more severe in the former case.

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With this background, Figure 1 and hence the trends in $\Delta H_{\text{enolate}}$ noted at the beginning of this section can now be understood. Electronegative atoms stabilize both the enolate and oxo form, while basic lone pairs stabilize only the oxo form. Thus, enolate formation is relatively favorable for {F}, but significantly worse for {OH, NH₂}. When the attached atom has a partial positive charge, {CF₃, CHO, CN, NO₂}, inductive stabilization is more important and electrostatic destabilization is less important in the enolate versus the oxo form. Thus, enolate formation is thermodynamically most facile for these groups.

2. Comparison to Other Systems. As stated in the Introduction, it is desirable not only to understand substituent effects on enolate formation, but also to relate this reaction to previously studied systems. Every enolate product, H₂C=C(O⁻)X, has two functional groups, the carbon-carbon double bond and the carbon-oxygen anion single bond. Substituent effects on both functional groups have been studied, the former by Wiberg and Rablen,²⁸ the latter by Rosenberg.²⁹ Data for the corresponding isodesmic reactions are listed in Table 1 for ethene derivatives under $\Delta H_{\text{H}_2\text{CCHX}}$ (9), and for alkoxides under $\Delta H_{\text{CH}_3\text{CH(O}^-)\text{X}}$ (4). A crude comparison of these values shows that $\Delta H_{\text{H}_2\text{CC(O}^-)\text{X}}$ (2), the isodesmic reaction for enolates, is similar to reaction 4, but not to reaction 9. Both reactions 2 and 4 follow the ordering {F > OH > NH₂}, while reaction 9 is ordered {OH ~ NH₂ > F}.

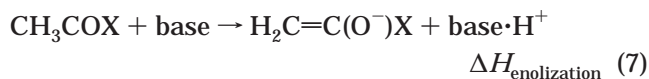


$$\Delta H_{\text{CH}_3\text{COX}} - \Delta H_{\text{CH}_3\text{CH(O}^-)\text{X}} = \Delta H_{\text{reduction}} \quad (5)$$

Quantitatively, a plot of $\Delta H_{\text{CH}_3\text{CH(O}^-)\text{X}}$ (4) vs $\Delta H_{\text{H}_2\text{CC(O}^-)\text{X}}$ (2) yields a straight line with a slope of 1.06, an intercept of 1.78 kcal/mol, and a correlation coefficient (*r*²) of 0.896 for the 11 groups common to both reactions {H, CH₃, NH₂, OH, F, CH₂CH₃, CHCH₂, CCH, CF₃, CHO, CN}. The goodness of the fit suggests that there is a qualitative similarity between substituent effects on enolates, analyzed in this paper, and on alkoxides, analyzed in ref 29. As with $\Delta H_{\text{H}_2\text{CC(O}^-)\text{X}}$, effects on $\Delta H_{\text{CH}_3\text{CH(O}^-)\text{X}}$ follow a simple rule: electron withdrawal is the only factor which raises $\Delta H_{\text{CH}_3\text{CH(O}^-)\text{X}}$; basic lone pairs have no effect. When the attached atom becomes more electronegative, $\Delta H_{\text{CH}_3\text{CH(O}^-)\text{X}}$ becomes increasingly positive {F > OH > NH₂ > CH₃}, which is similar to enolates. The ordering of $\Delta H_{\text{CH}_3\text{CH(O}^-)\text{X}}$ is inverted with respect to the *s* character on the attached carbon {CH₂-CH₃ > CHCH₂ ~ CCH}, compared to a modest, normal effect for enolates. The powerfully electron-withdrawing substituents {CF₃, CHO, CN} provide only modest stabilization in $\Delta H_{\text{CH}_3\text{CH(O}^-)\text{X}}$; {CN} is comparable to {NH₂} while {CF₃, CHO} are only slightly more stabilizing than {CH₃}. Again, this effect is similar to that seen for enolates. Presumably, there is electrostatic destabilization between the partially positive charges on the attached carbon of {CF₃, CHO, CN} and the carbon bound to oxygen. This effect counteracts the inductive effects of these groups for both enolates and ethoxides.

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Since substituent effects on $\Delta H_{\text{H}_2\text{CC(O}^-)\text{X}}$ and $\Delta H_{\text{CH}_3\text{CH(O}^-)\text{X}}$ are similar, the substituent effects on reactions 6 and 7 should also be related. Note that both reactions start with the same compound and that the enthalpy of the reagent, "H⁻" or base, is canceled when looking at relative energies. Thus, relative energies for reaction 6 are equal to reaction 5, and those for reaction 7 to reaction 3. A plot of reaction 3 versus reaction 5 yields a slope of 0.98, an intercept of -2.73 kcal/mol, and a correlation coefficient (*r*²) of 0.866 for the 11 common substituents {H, CH₃, NH₂, OH, F, CH₂CH₃, CHCH₂, CCH, CF₃, CHO, CN}. While the agreement is not spectacular, it is interesting that these two very different reactions behave similarly when perturbed by a wide variety of substituents. This similarity may become even more significant if hydride reductions turn out to be representative of anionic addition reactions to carbonyls, as I suggested earlier.²⁹

Enols. 1. Substituent Effects on Enol Formation. The energies for enolization of CH₃COX to H₂C=C(OH)X are listed in Table 1 under the heading ΔH_{enol} and are relative to {H}, which is set to 0.0 kcal/mol. In all cases the most stable conformation of the enol³⁰ is used for the calculation of ΔH_{enol} . The absolute value for enol formation of acetaldehyde is calculated to be 11.2 kcal/mol, reasonably close to the experimental gas-phase value of 9.1 kcal/mol.¹⁴ Interestingly, Lemal has determined ΔH_{enol} for several highly fluorinated ketones.³¹ Unfortunately, these values are strongly affected by the fluorine atom directly attached to the carbon-carbon double bond³² and cannot be directly compared to data in the present study.

Unlike enolates, substituent effects on enol formation do not follow a simple pattern. Substituents fall into three distinct energy groupings (note that positive values of ΔH_{enol} indicate that enol formation is energetically unfavorable relative to acetaldehyde). Three substituents {NH₂, OH, F} have ΔH_{enol} values of 14.6-16.5 kcal/mol. These data are consistent with the difficulties of experimental observation of these enols.^{3,4} Between -2.0 and 1.6 kcal/mol, lie the ΔH_{enol} values of several diverse substituents {CH₃, CF₃, CN, NO₂, CH₂CH₃, CHCH₂, CCH}. Finally, for {CHO}, enol formation is favored by 7 kcal/mol relative to acetaldehyde. As with enolates, these data can be understood using the analogous thermodynamic cycle illustrated in Figure 2.

Figure 2 makes use of the isodesmic reactions for CH₃-COX (1), discussed above, and H₂C=C(OH)X (8), written below. The latter reaction describes the effects of substituents on vinyl alcohol and is listed in Table 1 under the heading $\Delta H_{\text{H}_2\text{CC(OH)X}}$. Note that positive values of

(30) Enol geometries are listed in the Supporting Information. Geometries and energies of minor isomers are available upon request from the author.

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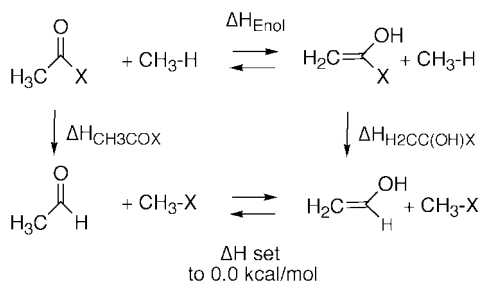
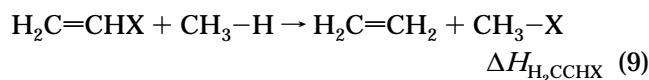
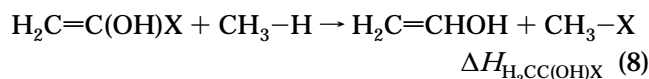


Figure 2. Thermodynamic cycle showing the connection between the isodesmic reactions, $\Delta H_{H_2CC(OH)X}$ and ΔH_{CH_3COX} , and the energy of enolization of CH_3COX , ΔH_{enol} , relative to that of CH_3CHO .

$\Delta H_{H_2CC(OH)X}$ indicate the substituent is stabilizing relative to {H}. In an effect seen in the analysis of the carbonyl group,²⁷ attachment of an electronegative atom {NH₂, OH, F} stabilizes the enol form relative to {H} due to electrostatic attraction between the oxygen bound carbon and the attached atom. Since the values of $\Delta H_{H_2CC(OH)X}$ for {NH₂, OH} are comparable to {F}, basic lone pairs must also stabilize the enol form. Presumably, this stabilization arises from the delocalization of electron density from the lone pairs into the π system. The effects of hybridization of the attached carbon are small in magnitude and do not follow a simple pattern {CHCH₂ > CH₂CH₃ ~ CCH}. Conjugation with an sp², but not an sp center, mildly stabilizes the enol form. When nonpolar C–H or C–C bonds of the attached carbon are replaced by polar bonds, the value of $\Delta H_{H_2CC(OH)X}$ is lowered as evidenced by the differences between {CF₃ (–10.0)} and {CH₃ (8.8)} and between {CN (0.6)} and {CCH (5.1)}. Presumably, electrostatic repulsion between the oxygen bound carbon and the attached carbon of X destabilizes the enol form. Yet the values of $\Delta H_{H_2CC(OH)X}$ for {CHCH₂ (9.5)} and {CHO (11.3)} do not follow this pattern, probably due to a stabilizing hydrogen bond in the latter.



With this background, Figure 2 and the trends in ΔH_{enol} noted at the beginning of this section can now be rationalized. Both the enol and oxo forms are stabilized by attachment of an electronegative atom and by π donation, with significantly larger effects seen for the oxo form. Thus, {NH₂, OH, F} all have large, positive values of ΔH_{enol} . The hybridization of the attached carbon, as seen in the series {CH₂CH₃, CHCH₂, CCH}, has a small effect on both the enol and oxo forms, resulting in values of ΔH_{enol} near 0.0 kcal/mol. When the attached atom is bonded to electron-withdrawing substituents {CF₃, CN, NO₂}, both the enol and oxo forms receive little net stabilization due to electrostatic repulsion between the oxygen bound carbon and the attached atom. Again, the values of ΔH_{enol} are near 0.0 kcal/mol. The anomalous negative value of ΔH_{enol} for {CHO} is due to a stabilizing hydrogen bond in the enol form.

2. Comparison to Other Systems. As with enolates, it is desirable not only to understand substituent

effects on enol formation, but also to relate this reaction to previously studied systems. Below, substituent effects on enols will be compared to those on alkenes, a system thoroughly analyzed by Wiberg and Rablen.²⁸

To examine the effect of substituents on ethene derivatives, Wiberg and Rablen used isodesmic reaction 9 above. These values were recalculated using the G2-(MP2) methodology for consistency with this work and appear in Table 1 under the heading ΔH_{H_2CCHX} . Wiberg and Rablen noted that substituent effects on C=C bonds are qualitatively similar to those on C=O bonds. All effects are significantly larger in magnitude for C=O due to this group's relatively large polarization. Thus, both alkenes and carbonyls are stabilized by electrostatic attraction and π donation in {NH₂, OH, F}, and both are destabilized by electrostatic repulsion between the partially positive carbons of the C–X bond in {CF₃, CN, CHO}.

When an alcohol group is attached to an alkene to form an enol, there is the potential for both qualitative and quantitative changes in the effects of substituents. A plot of $\Delta H_{H_2CC(OH)X}$ versus ΔH_{H_2CCHX} yields a straight line with a slope of 1.35, an intercept of 1.31 kcal/mol, and a correlation coefficient (r^2) of 0.981 for the 11 substituents {H, CH₃, NH₂, OH, F, CHCH₂, CCH, CF₃, CHO, CN, NO₂}. The goodness of the fit and the slope of the plot, respectively, show that substituent effects on enols parallel those on ethene derivatives, but are about 35% stronger for the former. The alcohol group of the enol polarizes the carbon–carbon double bond to a level intermediate between ethene and C=O. This ordering of the double bond polarity is mirrored in the magnitude of substituent effects, with the largest effects seen for the highly polar C=O bond. The conclusions from this section are qualitatively similar to those reached earlier by HKFS using the HF/6-31G*/HF/3-21G level of theory.¹⁹

Conclusions

In the introduction it was noted that there are many more data on enolates of carboxylic acid derivatives than on the corresponding enols. With data from this work, these compounds can now be compared. Enolates are stabilized solely by electron withdrawal and in this respect behave very much like ethoxides, the double bond of the former having only a small effect. This relationship leads to the surprising conclusion that substituent effects on both the deprotonation of and hydride addition to carbonyl compounds are similar. Substituent effects on enols are qualitatively similar to those on both carbonyls and ethenes. The hydroxyl group of the enol polarizes the double bond making these effects larger than for ethene, but still considerably smaller than for the carbonyl group. Curiously, enolization is made more difficult by groups which stabilize the enol form, as these same groups stabilize the oxo form to an even greater extent. From this study, it is apparent that substituent effects on enolates and enols are very different.

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Supporting Information Available: Tables of energies and optimized MP2=full/6-31 g* geometries (14 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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