Computational Study on the Effects of Substituents and Functional Groups in the Isomerization of 1- and 2-Substituted Propenes, Acetaldimines, and Aldehydes

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We have performed ab initio molecular orbital calculations on 1- and 2-substituted propenes, acetaldimines, and aldehydes — $H_3CC(X)=Y$ and $XCH_2CH=Y$ (Y = CH_2, NH, O; X = H, CH_3, NH_2, OH, F) — to investigate the effects that substituents and functional groups have on their isoelectronic (except X = H) tautomerism. Structures for all stationary points (keto forms, enol forms, and transitions states) were optimized at the HF/6–31G**, MP2(full)/6–31G*, and B3LYP/6–31G** levels of theory and were characterized by frequency calculations. We performed intrinsic reaction coordinate (IRC) calculations at the HF/6–31G** level of theory to connect the transition structures with their local minima along the reaction path. In the transition structures, the migrating H4 atom is slightly out of plane, with a dihedral angle H4–C2–C1–Y3 (d4) of $< 12°$. In the keto–enol and imine–enamine series, the keto forms are thermodynamically more stable than their counterparts by ca. 30 kcal·mol^{-1} regardless of the site of substitution. In the 2-substituted propene (Y = CH_2) series, the enol forms are lower in energy than the keto forms by ca. 3–10 kcal·mol^{-1}. There is a very good linear correlation between the relative energies and the electronegativity (Pauling scale) of the non-hydrogen atom in Y of the functional group C=Y; the coefficient of the linear regression ranges from 0.98624 to 0.99963 for the six tautomeric series at the G2 level of theory. We explain the effects that the substituents have on the relative energies in terms of the changes in bond dissociation energies (by means of isodesmic reactions) and the dispersion of the charge through resonance effects (NBO analysis). These "enolization" processes all have rather high activation energies of 56–78 kcal·mol^{-1} at the G2 levels of theory.

Introduction

Tautomers are compounds possessing distinct structures that arise from migration of a hydrogen atom. The best known example of tautomerism is that between a carbonyl compound (keto form) and a vinyl alcohol (enol form),[1] but other common examples include imine−enamine,[2] oxime−nitroso,[3] hydrazo−azo,[4] and phenol−keto[5] isomerization. Erlenmeyer[6] reported in 1881 that vinyl alcohols rearrange upon their formation to form aldehydes and ketones. In 1906, Kohler[7] added C_6H_5MgBr to an unsaturated ketone and isolated a crystalline enol. Further studies on the synthesis of simple enols were reported by Fuson[8] and Bosnich[9] in the early 1940s. The simplest enol, vinyl alcohol, was observed in 1967 by Hay and Lyon[10] upon oxidation of dideuterioacetylene in a mass spectrometer. Blank and Fischer[11] confirmed this finding by NMR spectroscopy in 1973. In addition, Saito[12] identified vinyl alcohol in 1976 as a reactive intermediate during the pyrolysis of cyclobutanol. Although both keto and enol tautomers can be found in the laboratory, the former are generally thermodynamically more stable than the latter by ca. 20 kcal·mol^{-1}.[13] This energy difference implies a small equilibrium constant, K_E = [enol]/[keto] $< 10^{-8}$, for the rapid equilibrium between the two forms and suggests that the enol forms are possible intermediates appearing during the preparation of aldehydes and ketones. In many organic reactions (e.g., electrophilic substitutions of carbonyl-containing compounds, oxy-Cope, Conia, and Carrol rearrangements, and *retro*-Diels−Alder reactions) the enolization process is the rate-determining step, and its activation energy is altered by the presence of substituents. In an analogous tautomerism process, imines exist in a rapid equilibrium with enamines. The structures of the parent tautomers, acetaldimine and vinylamine, which are the products of the pyrolysis of ethylamine,[14] have been determined by Lovas[15] by microwave spectroscopy.

In addition to experimental studies, ab initio molecular orbital calculations have been carried out in order to study: (1) parent keto−enol[16] and imine−enamine tautomerism, and (2) the effects of substituents on the relative stabilities and activation energies during the tautomeric interconversion.[17] At the G-1[18] level of theory, acetaldehyde is found

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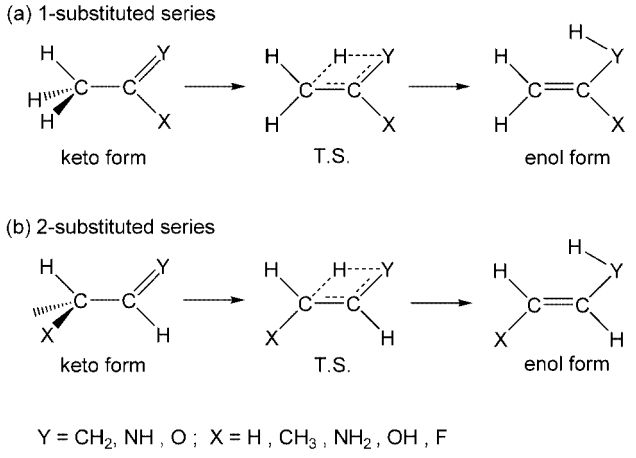
to be 47.0 kcal·mol^{-1} lower in energy than vinyl alcohol; in the imine−enamine case, the relative energy is only 3.8 kcal·mol^{-1} in favor of acetaldimine.[19] Theoretical studies exhibit the general trend that the computed relative energies and activation energies in imine−enamine interconversions are both lower than those in the corresponding keto−enol processes. We have reported[20] our studies of substituent effects in the tautomerism of acetaldimine at the MP4/6−31++G**//MP2(full)/6−31G* and G-2 levels. At the MP2(full)/6−31G* level we observed that the energy differences between tautomers and the barriers to their interconversion in the tautomerism of 2-substituted imines and enamines are both lower than those of the corresponding keto−enol processes by ca. 8 and 3 kcal·mol^{-1}, respectively. In these equilibria, the keto forms and imines are both lower in energy than their tautomers. In addition, we found that the relative energy, with respect to the keto form, and the barrier to enolization are both lower by ca. 12 and 5 kcal·mol^{-1}, respectively, for 2-substituted aldehydes relative to the 1-substituted series.

To extend these studies, we have investigated 1- and 2-substituted propenes and 1-substituted acetaldimines (Scheme 1). We consider acetaldimines and propenes to have keto forms and ascribe enol structures (forms) to their tautomeric counterparts.



Y = CH_2, NH , O ; X = H , CH_3 , NH_2 , OH , F

Scheme 1

In this paper we report the effects of substituents and functional groups on the tautomeric interconversions of $H_3CC(X)=Y$ and $XCH_2C(H)=Y$, where X = H, CH_3, NH_2, OH, or F and Y = O, NH, or CH_2. Our goal is to probe further the trends found in the relative energies and activation energies of tautomerization reactions. We correlate our computed results to the bond energies and the electron-donating and -withdrawing properties of substituents with respect to: (1) the type of substituent, (2) the type of functional group, and (3) the position of the substituent relative to the functional group.

Computational Methods

Ab initio molecular orbital and density functional theory (DFT) calculations were carried out for all geometry optimizations at the Hartree−Fock and B3LYP[21] levels of theory with use of the 6−31G**[22] basis set, while the geometries used in the G2 calculations are optimized at the MP2(full)/6−31G* level of theory. Harmonic vibrational frequency calculations were computed at the same level of theory as the geometry optimizations in order to characterize the stationary points as local minima (equilibrium structures) or first-order saddle points (transition structures) on the potential energy surface and to evaluate the zero-point vibration energy (ZPVE). Calculations of intrinsic reaction coordinates (IRC)[23] were performed at the HF/6−31G** level of theory to establish the connection between the transition structures and the corresponding local minima along the reaction pathways. For better understanding of the interaction of the atoms during a tautomerism process, we have used natural bond orbital (NBO)[24] analysis to obtain data for: (1) the evaluation of bond order, (2) the stabilization energy, and (3) the natural population analysis (NPA). The effects of the substituents and functional groups on the bond dissociation energies[25] were studied by means of isodesmic reactions.[26] To examine the local charge flow within a species along the reaction path, we implemented IRC calculations to obtain the atomic charges from the MPA at the HF/6−31G** structures. The Gaussian 94[27] and Gaussian 98[28] package programs have been used throughout this study.

Results and Discussion

The trends existing between the geometries, relative energies, and activation energies calculated at the various levels of theory in this study are similar, and so we report only the results of calculations at the G2 level of theory unless otherwise stated.

A. Geometries

Figure 1 displays the optimized geometries and the point groups of the stationary points along the path of tautomeric interconversion leading to the enol structures on the potential energy surface for the parent keto structures of the 1-substituted $H_3CC(X)=Y$ and 2-substituted $XCH_2CH=Y$ compounds, in which Y = O, NH, and CH_2 and X = H.[29] The general trends observed suggest that there are definite similarities in all these tautomerism processes. All local minima (keto forms and enol forms) have either C_s or C_1 symmetry, while hydroxyvinyl alcohol (1-substituted series: Y = O and X = OH: i.e., the enol form of acetic acid) has the highest symmetry (C_{2v}). The transition structures all have C_1 symmetry. During the interconversion between tautomers, we observe the following average changes of the most relevant geometry parameters optimized at the MP2(full)/6−31G* level of theory. On proceeding from the keto structures to the transition structures, the C1−Y3 (r3) and

C2−H4 (r4) bonds lengthen by 0.068 and 0.405 Å, respectively, and the bond angles H4−C2−C1 (a4) decrease by 39.8°; from the transition structures to the enol structures, the C1−C2 (r2) bond lengths and the H4−Y3−C1 (a4′) angles decrease by 0.069 Å and 33.1°, respectively, and the lengths of the Y3−H4 bonds (r4′) increase by 0.311 Å. The migrating H4 atom in every transition structure is slightly out of plane, with the H4−C2−C1−Y3 (d4) dihedral angles calculated to be < 12°. The enolization process is characterized by the breaking of C1=Y3 double bonds in the keto forms and the formation of C1=C2 double bonds in the enol forms. As we see in Figure 2, the substituents exert virtually no effect on the C=C bond lengths of the enols in the 1-substituted series; conversely, the effect of the substituent on the C=Y bond length is significant in the keto forms. In the 2-substituted series, the substituents have little effect either on the C=C double bonds in the enol forms or on the C=Y double bonds in the keto forms.

The computed structural data are in good agreement with the available experimental data obtained from electron diffraction (ED) and microwave spectroscopy (MV). It can be seen that the deviations in r2 (C1−C2), r3 (C1=O3), and a3 (C2−C1−O3) for the keto forms of the 1-substituted aldehydes series range from 0 Å to 0.014 Å, 0.001 Å to 0.032 Å, and 0° to 4°, respectively.[30]

B. Relative Energies

The relative energies (E_r) of enol forms with respect to keto forms as determined at the G2 level of theory are listed

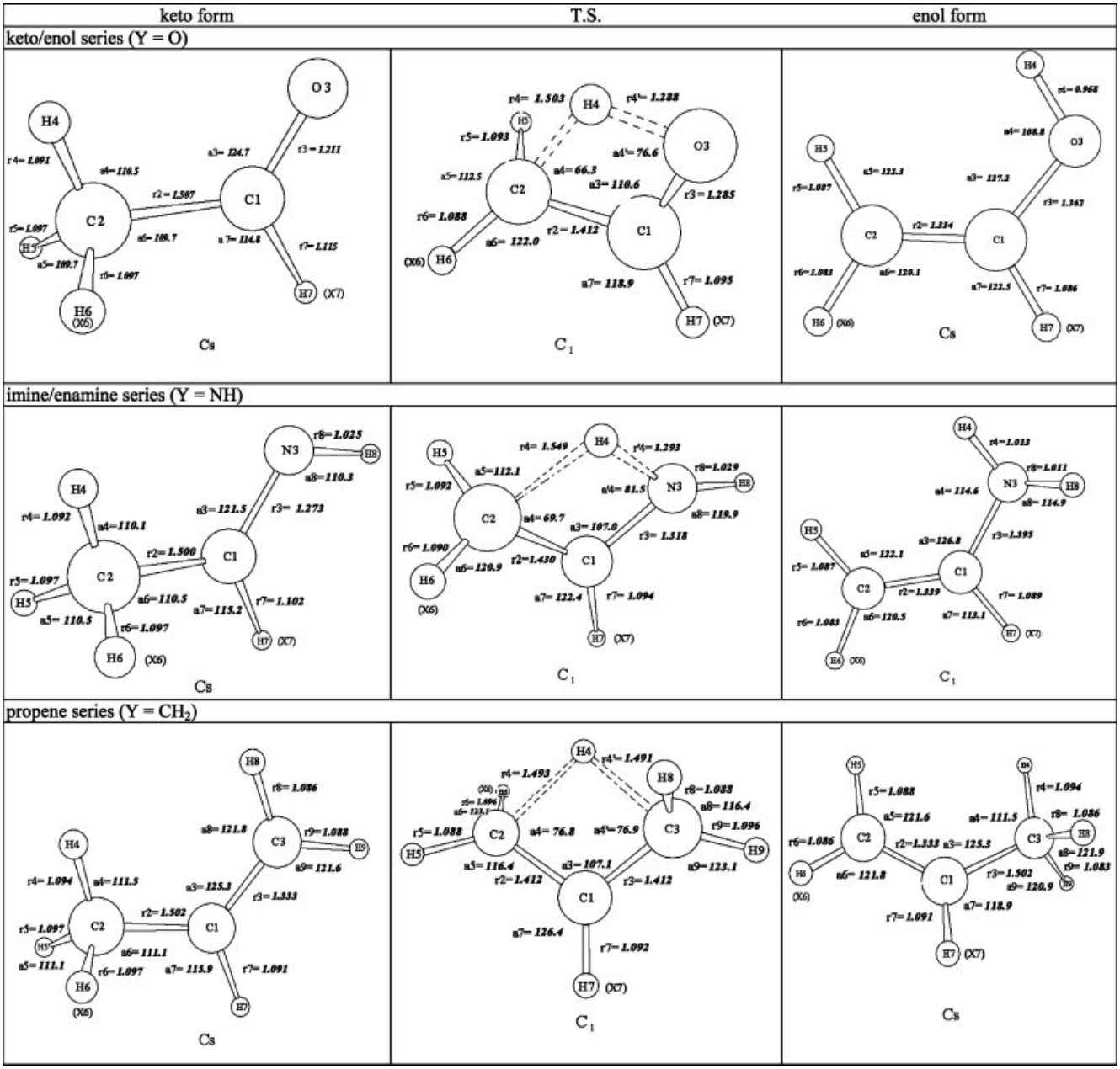


Figure 1. The optimized geometries (in Å and deg) of keto forms, transition structures, and enol forms of the parent systems (X = H) at the MP2(full)/6−31G* levels of theory

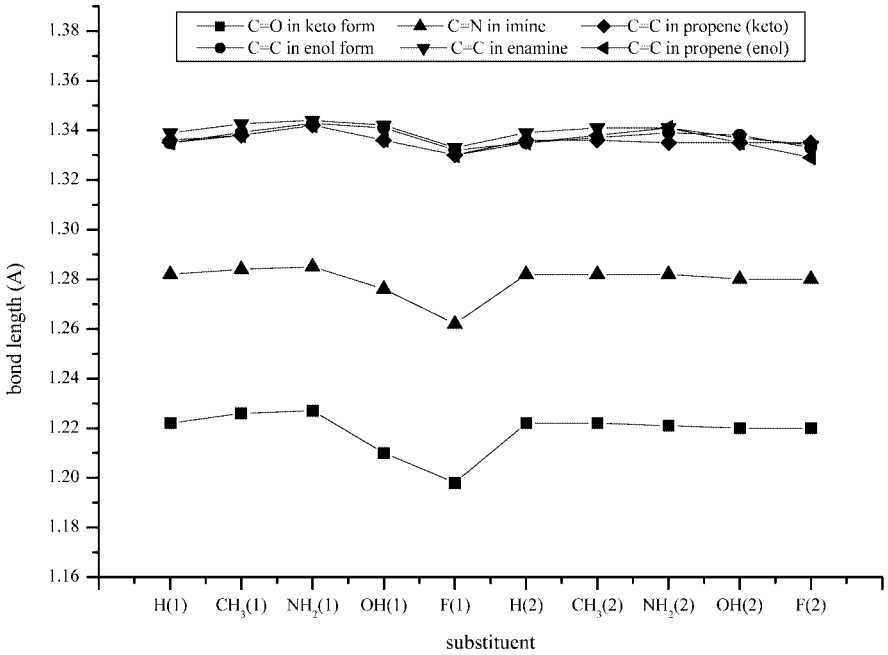


Figure 2. Bond lengths of C=Y and C=C at the MP2(full)/6−31G* levels of theory; the number in parentheses indicates the site of substitution

Table 1. The relative energies (kcal·mol^{-1}), activation energies (kcal·mol^{-1}), and the n_T values of the transition structures at the G2 level of theory

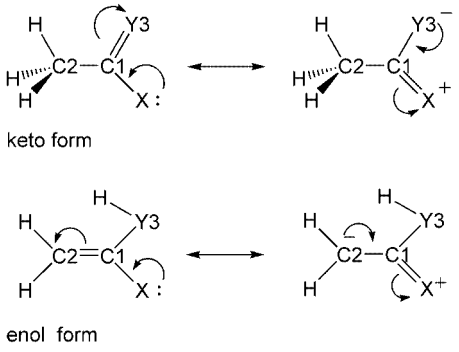
1-Substituted series X\Y	CH_2					NH					O				
	E_r [a]	E_a [b]	$\Delta G°$	$\Delta G^‡$	n_T	E_r	E_a	$\Delta G°$	$\Delta G^‡$	n_T	E_r	E_a	$\Delta G°$	$\Delta G^‡$	n_T
H	0.00	80.86	0.00	81.39	0.500	4.22	64.00	4.01	64.94	0.516	11.90[c]	66.62	11.54	68.16	0.546
CH_3	0.00	79.09	0.00	80.37	0.500	5.03	62.56	4.79	64.42	0.519	13.58	65.05	13.39	66.43	0.556
NH_2	0.00	69.86	0.00	72.25	0.500	9.79	58.99	9.36	60.88	0.542	25.32	64.09	25.97	66.13	0.622
OH	0.00	73.24	0.00	75.43	0.500	10.42	65.21	10.63	66.95	0.543	23.91	67.35	24.75	69.46	0.608
F	0.00	78.17	0.00	79.57	0.500	12.17	68.90	12.24	70.84	0.547	26.65	75.00	26.98	77.27	0.606
2-Substituted series X\Y	CH_2					NH					O				
	E_r	E_a	$\Delta G°$	$\Delta G^‡$	n_T	E_r	E_a	$\Delta G°$	$\Delta G^‡$	n_T	E_r	E_a	$\Delta G°$	$\Delta G^‡$	n_T
H	0.00	80.86	0.00	81.39	0.500	4.22	64.00	4.01	64.94	0.516	11.9	66.62	11.19	67.71	0.545
CH_3	−3.02[d]	77.39	−2.65	78.77	0.492	2.40	62.54	2.53	65.19	0.510	9.69	65.16	9.39	67.38	0.538
NH_2	−7.98	67.41	−7.64	70.24	0.474	2.15	59.55	2.55	62.42	0.510	9.62	63.05	9.47	65.33	0.539
OH	−6.39	69.14	−5.76	71.46	0.481	2.31	59.22	2.57	62.54	0.511	10.23	64.06	10.08	66.95	0.541
F	−3.23	71.43	−2.73	73.69	0.491	3.91	60.79	4.14	63.72	0.517	12.03	66.13	11.98	68.76	0.548

[a] The relative energy of the enol form with respect to the keto form. [b] The activation energy of enolization. [c] Experimental values 8.65 to 16.55 kcal·mol^{-1} (ref.[41]). [d] Experimental values −2.00 to −2.86 kcal·mol^{-1} (ref.[42]).

in Table 1.[31] The results indicate that the relative energies increase with increasing electronegativity of the functional group and that the effects of the substituents depend on the site of substitution. In the 1-substituted series, the substituents increase the relative energies; the reverse is true in the 2-substituted series.

B.1. The Effects of Functional Groups

A very good linear correlation exists between the relative energies and the electronegativity (Pauling scale)[32] of the non-hydrogen atom in Y in the functional group C=Y. The values of correlation coefficient (a measure of goodness-of-fit) of the linear regression lie in the 0.98624−0.99963 range for the six tautomeric series. An increase in the electronegativity of the non-hydrogen atom in Y results in strengthening of the C1=Y3 double bond and stabilization of the keto form. We also note that the electronegativity of Y and the position (1- or 2-substitution) of the substituent group X have large influences on the ability of the C1=Y3 double bond to delocalize electronic charge, which is a feature that affects the relative energies of the tautomers.



Scheme 2

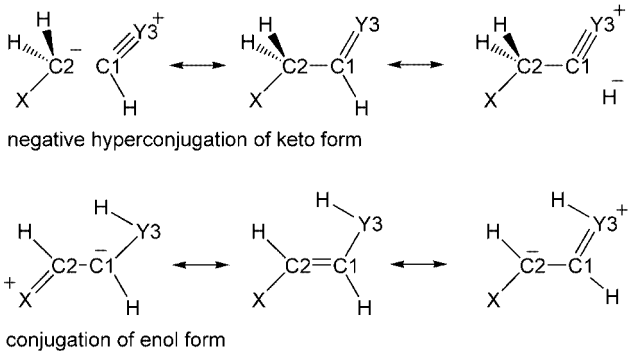
In the 1-substituted series, depicted in Scheme 2, the substituent group in the keto form is attached to the C=Y double bond; in the enol form it is directly bonded to the C=C double bond.

The C=Y groups are π-electron acceptors in all cases, with π-withdrawing ability increasing in the order $C{=}CH_2 < C{=}NH < C{=}O$, which is the same order as the increase in electronegativity: calcd. C < N < O. π-Electron donation from the substituent group X to the functional group C=Y stabilizes the keto form. As a result, with the exception of Y = CH_2, in which the keto form and enol form are identical, the keto forms are more stable than the corresponding enol forms when the non-hydrogen atom in Y of the functional group C=Y is more electronegative. The stabilization energies presented in Table 2, obtained from NBO analyses, reflect the π-withdrawing abilities of the C=Y groups. We see that the more electronegative Y groups tend to withdraw more electron density from the lone pair of electrons (LP_X) in the substituent X to the antibonding orbital of the C=Y double bond π*(C=Y). This situation results in the stabilization energies of $LP_X \rightarrow \pi^*(C{=}Y)$ increasing in the sequence $CH_2 < NH < O$, which is also the order of increasing electronegativity of C, N, and O atoms.

Table 2. Stabilization energies of $LP_X \rightarrow \pi^*(C{=}Y)$ in the keto forms and $LP_X \rightarrow \pi^*(C{=}C)$ in the enol forms in the 1-substituted series

$LP_X \rightarrow \pi^*(C{=}Y)$ in keto form				$LP_X \rightarrow \pi^*(C{=}Y)$ in enol form		
X\Y	O	NH	CH_2	O	NH	CH_2
H	0	0	0	0	0	0
CH_3	16.41	16.28	12.74	15.54	14.02	12.74
NH_2	90.08	61.67	43.36	38.44	45.29	43.36
OH	69.83	63.01	46.50	57.36	40.72	46.50
F	54.20	46.38	8.45	42.54	31.47	8.45

In the 2-substituted series, the substituents X in this series are bonded to C2, which is part of the C=C double bond in the enol forms, whereas in the keto forms they are not attached directly to the double bond. The data obtained from NBO calculations suggest that the stabilization of the enol structure results from conjugation (hyperconjugation for X = CH_3) between the π bond and the lone pairs of electrons of the X and Y atoms. The keto form, on the other hand, is stabilized mainly by a negative hyperconjugation effect between the functional group C=Y and the C2−C1 and C1−H bonds (Scheme 3).



Scheme 3

Although delocalization effects are more stabilizing in an enol form than in its keto counterpart (Table 3), Table 1 indicates that the latter tautomers are lower in energy than the former (except, of course, when Y = CH_2) because of the bond energies of the double bonds in each tautomer. The C1=Y3 bond energy of the keto form is 20−30 kcal·mol^{-1} higher than that of the C1=C2 bond in the enol form.[33] This finding demonstrates that the bond energy property, which favors the keto form, dominates more than the delocalization effects. As summarized in Table 3, the effects of conjugation or hyperconjugation are stabilizing for the enol forms and increase for Y in the sequence $NH < CH_2 < O$, except for electropositive substituents (X = CH_3 and H). For the series with Y = O, both tautomers are approximately equally stabilized by the delocalization of the double bonds. This feature, combined with the effects of the bond energies, which increase for Y in the sequence $CH_2 < NH < O$, accounts for the largest relative energies being observed in the series of keto−enol tautomerizations. In the series with Y = CH_2, the delocalization effect has more impact on enol forms than on their corresponding keto tautomers. This phenomenon results in the smallest relative energies (enol−keto), among all the three series studied, being observed for the Y = CH_2 series.

In summary, the relative energies (enol−keto) in the 2-substituted series are smaller than those observed for the 1-substituted isomers. This phenomenon results because delocalization in the former series is more stabilizing for enol forms than for their keto tautomers (Table 3), which thereby reduces the energy difference between them. The opposite situation is true in the 1-substituted series and so the relative energies between keto and enol forms increase.

B.2. Effects of Substituents

We explain the effect of substituents on the relative energies in terms of the changes in bond dissociation energies and dispersion of charge through resonance effects. We dis-

Table 3. Stabilization energies in the 2-substituted series through π-electron donation of both the functional groups Y (in C=Y) and the substituents X

Enol form X\Y	O			NH			CH_2		
	$LP_X \rightarrow \pi^*(C=C)$	$LP_Y \rightarrow \pi^*(C=C)$	Sum	$LP_X \rightarrow \pi^*(C=C)$	$LP_Y \rightarrow \pi^*(C=C)$	Sum	$LP_X \rightarrow \pi^*(C=C)$	$LP_Y \rightarrow \pi^*(C=C)$	Sum
H	0.00	43.88	43.90	0.00	25.90	25.90	0.00	13.34	13.34
CH_3	11.41	47.68	59.10	11.48	34.01	45.50	12.79	12.98	25.80
NH_2	45.70	49.12	94.82	4.47	35.24	39.70	33.91	11.48	45.40
OH	41.75	41.74	83.50	15.36	23.64	39.00	37.33	10.41	47.70
F	30.63	46.36	77.00	27.87	15.27	43.10	33.96	12.36	46.30
Keto form X\Y	**O**			**NH**			**CH_2**		
	$LP_Y \rightarrow \sigma^*(C-C)$	$LP_Y \rightarrow \sigma^*(C-H)$	Sum	$LP_Y \rightarrow \sigma^*(C-C)$	$LP_Y \rightarrow \sigma^*(C-H)$	Sum	$LP_Y \rightarrow \sigma^*(C-C)$	$LP_Y \rightarrow \sigma^*(C-H)$	Sum
H	26.26	29.64	55.90	3.62	16.33	19.95	7.42	6.02	13.40
CH_3	25.80	29.96	55.80	3.52	16.54	20.10	7.41	6.13	13.50
NH_2	26.97	29.01	56.00	3.81	16.31	20.10	7.41	6.20	13.60
OH	27.78	28.64	56.40	4.18	16.39	20.60	7.30	6.14	13.40
F	28.23	28.66	56.90	4.52	16.6	21.10	7.20	6.20	13.40

cuss the former by means of isodesmic reactions and the latter by way of NBO analysis.

B.2.1. Isodesmic Reactions

Figure 3 displays the changes in the C−X bond dissociation energies calculated from the isodesmic reactions depicted in Scheme 4.[34] As Figure 3 indicates, the effect on the relative C−X bond dissociation energies of the substituents X in the 2-substituted series is small for the keto form, but large for the enol form. In the 1-substituted series, significant substituent effects are observed on the relative C−X bond dissociation energies in both the keto and enol forms, but the effect on the former surpasses that on the latter. That is to say, the keto forms in the 1-substituted series are more strongly stabilized by substituents than the enol forms and, therefore, there is a larger increase in the relative stabilities of these tautomers. The opposite is true in the 2-substituted series: the substituents stabilize the enol structures more than they do the keto forms. This phenomenon results in a decrease in their relative energies, but to a lesser extent than the increase in the 1-substituted series.

B.2.2. Natural Bond Orbital (NBO) Analysis

In the 1-substituted series, the substituent groups in this series function as π-electron donors to the C1=Y3 double bonds of the keto forms and to the C1=C2 double bonds of the enol forms. Since the former are better π-electron acceptors than the latter, the substituents stabilize the keto forms more than they do the enol isomers. This fact results in an increase in the relative energies. Table 2 displays that, for the keto−enol tautomerism (Y = O), the order of π-electron-donating ability is $NH_2 > OH > F > CH_3 > H$.

As displayed in Scheme 5, the substituents act both as π-electron donors, through conjugation (a), and as σ-acceptors, through negative hyperconjugation (b). These π- and σ-electronic effects are all stabilizing, with the latter effect being dominant when X is highly electronegative, such as F and OH (Table 4). As a result, the relative energies in the keto-enol series increase in the sequence $H < CH_3 < OH < NH_2 < F$ and in the imine−enamine series in the order $H < CH_3 < NH_2 < OH < F$. For the 1-substituted series with $Y=CH_2$ the keto and enol forms are identical.

In the 2-substituted series, π-electron-donating substituents are more stabilizing to enol forms than they are to keto forms. The π-electron-donating and stabilizing properties of the substituents increase in the sequence $H < CH_3 < F < OH < NH_2$, which is approximately the reverse of the order of the magnitudes of the relative energies for the three tautomeric series (Y = O, NH, and CH_2) (Table 1). The tautomeric interconversion in the 3-X-propene (keto form)/1-X-propene (enol form) series (Y = CH_2) is simply a migration of the π bond between two carbon−carbon bonds, while in the other two series (Y = O and NH) the migration of the double bond involves heteroatoms. Since bond energy is not a factor when Y = CH_2, the relative energies in this series of tautomeric pairs are determined only by the π-electron-donating properties of the substituents. This situation results in this series being the only one in which the tautomeric interconversions have negative relative energies (i.e., the enol forms are lower in energy than the keto forms). The absence of lone pair electrons in the functional group CH_2 prevents the keto forms from being stabilized by the effect of negative hyperconjugation, but substituents that act as π-electron donors significantly stabilize the enol forms. The negative relative energies of the enol forms with respect to the keto forms therefore increase with respect to X in the order $H < CH_3 < F < OH < NH_2$, which is also the sequence of increasing π-electron-donating characteristics of the substituents. Analysis of NBO calculations

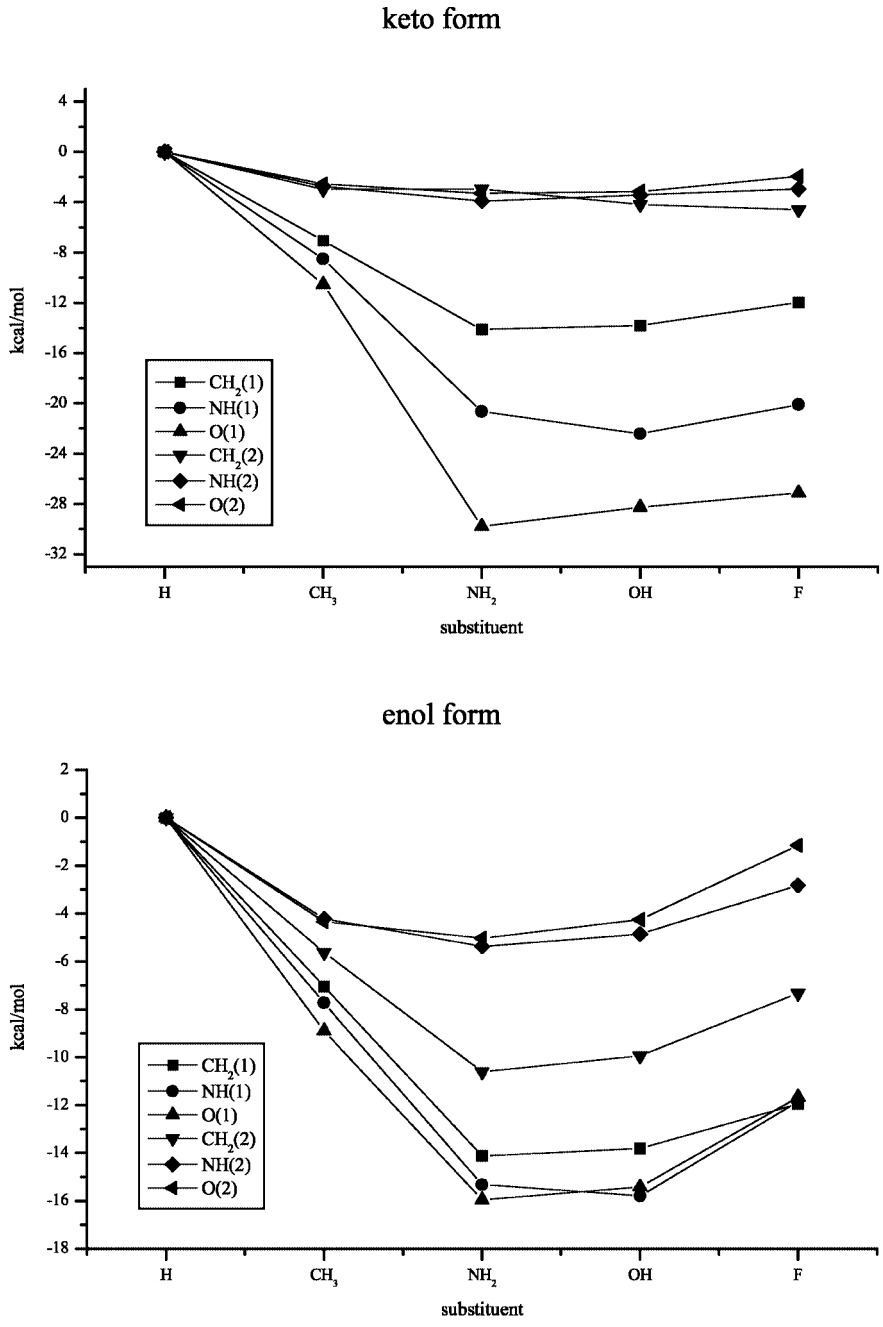
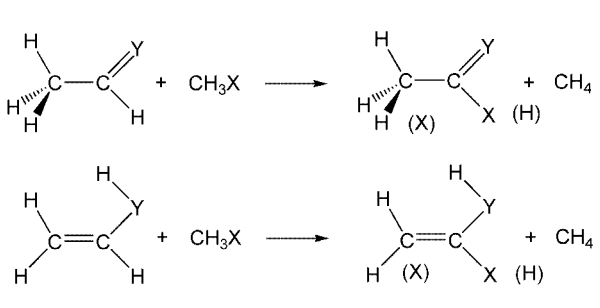
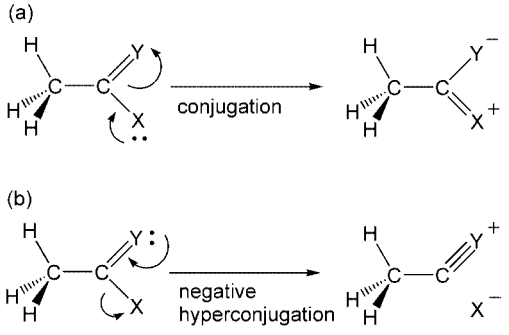


Figure 3. Bond energies computed at the G2 level of theory for the isodesmic reaction depicted in Scheme 4



Scheme 4



Scheme 5

Table 4. The stabilization energies (kcal·mol^{-1}) of the negative hyperconjugation $LP_Y \rightarrow \sigma^*(C1-X)$

X\Y	Y = O	Y = NH
F	61.91	31.25
OH	47.18	28.04
NH_2	35.41	22.73
CH_3	29.97	18.14
H	29.64	16.33

shows that there are good correlations between the stabilization energies and the bond orders of the C1=C2 and C1=C3 units in the enol and keto forms, respectively. As we see in Figure 4,[35] the substituents stabilize the enol forms over the keto forms and better delocalize (reduce the bond order of) the C=C double bonds in the former relative to the latter. We note that the magnitude of the influence that the substituents X exert on increasing the stabilization energy and decreasing the bond order of the C=C double bonds in the enol forms is $H < CH_3 < F < OH < NH_2$, which is the sequence of the negative relative energies.

B.2.3. Natural Population Analysis (NPA) and Mulliken Population Analysis (MPA)

Natural orbital analysis reveals trends in the changing degree of negative charge on relevant atoms in a molecule. Examination of the natural population analysis reveals[36] that, for the 1-substituted series, the negative charge on the Y3 atom and the positive charge on the migrating H4 increase as a result of π donation from the adjacent substituent X according to the sequence $H < CH_3 < F < OH < NH_2$ for the keto−enol and propene−propene series, and $H < CH_3 < F < NH_2 < OH$ for the imine−enamine series. This observation is in agreement with the order of the π-donating ability of the substituent, as is presented in Table 2 from the NBO analysis. In contrast, the substituents of the 2-substituted series exert little effect on the negative charge on the distant Y3 atom in the keto form. From the results of the IRC calculations, for all of the tautomerism profiles, we observed[37] similar trends for the electronic charges of relevant atoms at stationary points along the reaction pathway. Figure 5 presents the Mulliken population analysis profile for the parent species of the 1-substituted keto−enol tautomerization (Y = O, X = H). Note that the positive charge on the migrating hydrogen atom (H4) increases gradually from the keto form to the transition structure and then remains at about that level of charge as the structure proceeds to the enol form. This trend indicates that the "enolization" process can be classified as a type of proton transfer because the migrating hydrogen atom bears a partial positive charge.

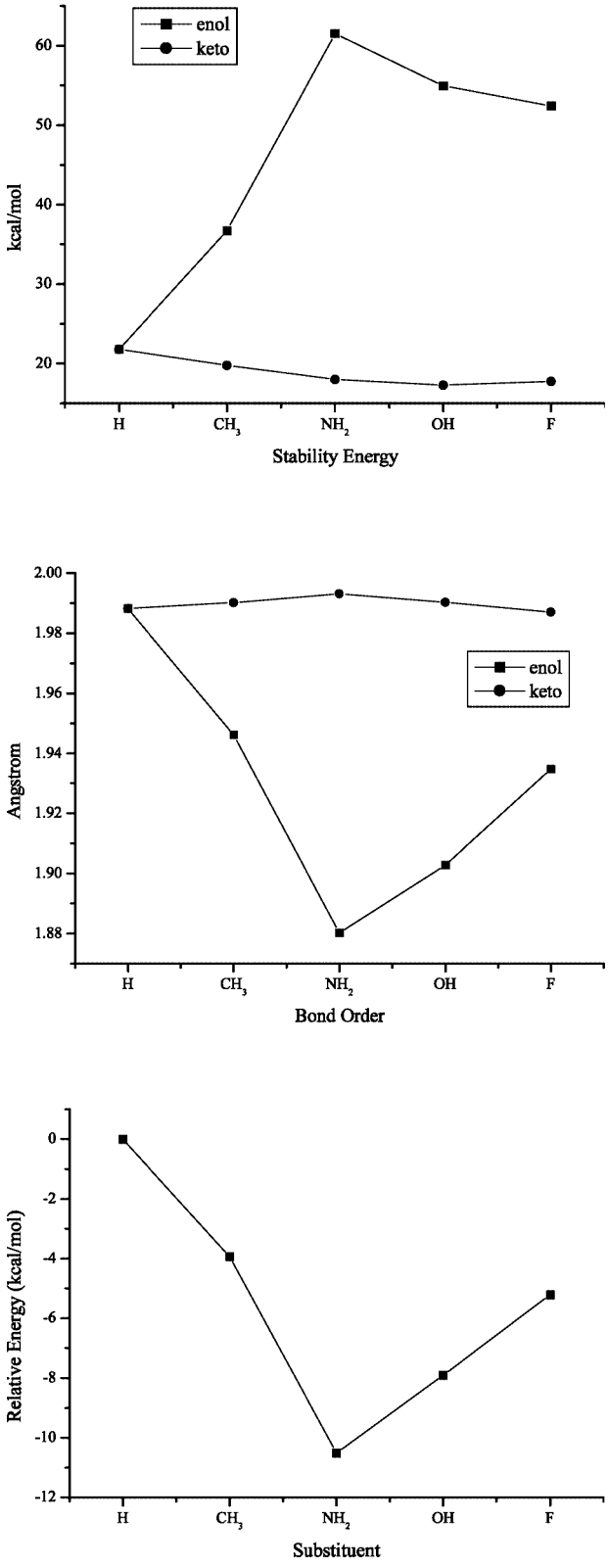


Figure 4. The substituent effect on the stabilization energies for X→π* (C=C), the bond orders of the C=C double bonds and relative energies

C. Activation Energies

The tautomeric interconversions of keto forms to enol forms for the six tautomeric processes examined in this study all possess rather high activation energies (56−78 kcal·mol^{-1}; Table 1). As a result, slow tautomeric

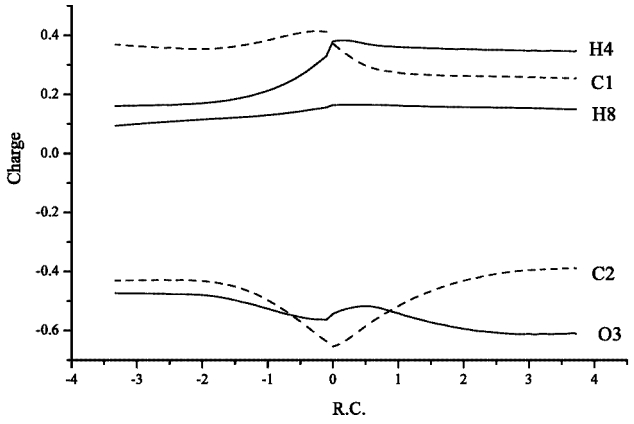


Figure 5. Reaction profiles depicting the electronic charges on the most relevant atoms during the keto−enol tautomerism in the 1-substituted series with Y = O, X = H

interconversions occur in the gas phase − even at 600 K − with rate constants, calculated by transition-state theory, of 10^{-16}–10^{-10} s^{-1}.

C.1. Effect of the Functional Groups

For a given substituent, the activation energies for conversion of the keto form to the enol form with respect to the Y unit of the functional group C=Y increase in the order NH < O < CH_2 in both the 1-and the 2-substituted series. In contrast to the good linear correlation between the relative energies and the electronegativities of the non-hydrogen atoms in the functional groups, there exists no linear correlation between the activation energies and electronegativity. We attribute this observation to the fact that the C=Y functional groups behave not only as π-electron acceptors to the substituents X but also as σ-electron donors to the C2−H4 bond. NBO analysis indicates that the substituent groups X exert a far greater effect on electron donation and withdrawal in the transition structure than they do in the keto form. Therefore, the activation energy for the "enolization" (i.e., the energy difference between the transition structure and the keto form) is determined mainly by the stability of the transition structure. A C1=Y3 double bond in which the non-hydrogen atom in Y3 has high electronegativity tends to become polarizing and π-electron-accepting. As a result, this unit stabilizes the transition structure and lowers the activation energy. Hence, by following the order of the electronegativities of the Y atoms, the activation energies would be expected to increase in the order O < NH < CH_2. The more electronegative O atom (relative to the N atom), however, also results in the C=O unit being a weaker σ-donor than the C=NH unit. This feature inhibits the migration of the H4 atom, increases the activation energy when Y = O, and results in the computed sequence of activation energies for the molecules with various functional groups.

A noteworthy feature is the observation of the characteristics of the transition structure and the Brønsted coefficient (β),[38] defined by Leffler as

$$\beta \equiv \frac{\partial E_a}{\partial E_r} = \frac{1}{2} + \frac{E_r}{2K_v}$$

and derived from the Marcus equation

$$E_a = \frac{1}{4}K_v + \frac{1}{2}E_r + \frac{E_r^{\,2}}{4K_v}$$

where E_a is the activation energy of "enolization", E_r is the relative energy of the enol form with respect to the keto form, and K_v is an intrinsic property of the reaction and is a constant for tautomeric processes in the same series. An examination of the relative energies (E_r) and the activation energies (E_a) listed in Table 1 clearly indicates that $E_r > 0$ and β > 1/2 for the 1- and 2-substituted keto−enol and imine−enamine series, $E_r < 0$ and β < 1/2 for the 2-substituted propene series, and $E_r = 0$ and β = 1/2 for the 1-substituted propene series. These values imply, in accordance with the Hammond postulate,[39] that: (a) for all keto−enol and imine−enamine series, the transition state is late and resembles the product (enol form) more than it does the reactant (keto form), (b) the 2-substituted propene series has an early transition state that resembles the keto form more than it does the enol form, and (c) the transition state equally resembles the reactant and product in the 1-substituted propene series. Hammond's postulate can also be interpreted in terms of the position of the transition structure along the reaction coordinate, n_T, as defined by Agmon:[40]

$$n_T = \frac{1}{2 - (\Delta G^\circ / \Delta G^\ddagger)}$$

where ΔG° is the difference in Gibbs free energy between the enol and keto forms and $\Delta G^\ddagger$ is the Gibbs free energy of activation for conversion of the keto form into the enol form.

In the 1-substituted series, the transition structure for Y = CH_2 resembles the keto and enol forms equally. When Y = NH or O, however, the late transition structure resembles the enol form more than its tautomeric counterpart. As we see in Table 1, the value of n_T for the various tautomeric series is 0.5 when Y = CH_2 and > 0.5 when Y = O or NH. The magnitude of the values of n_T, which indicate the degree of similarity between the transition structure and the product (enol form), increase with respect to Y in the order CH_2 < NH < O. This sequence implies that among the transition structures, those in the Y = O series have the smallest resemblance to their keto forms and the opposite is true for the transition structures in the Y = CH_2 series. This phenomenon results a relatively higher energy for the transition structures in the Y = O series and thus results in a higher barrier to enolization. The keto form in the 1-substituted series is more stable than the enol form because there is electron donation from the substituent to the polarizing C1=Y3 double bond and because the C=Y double bond (Y = O or NH) is more stable than the C=C double bond. Since a greater resemblance to the keto

component in the transition structure is a stabilizing feature and the transition state in the Y = O series has a lower keto form content (i.e., a greater value of n_T) than is observed in the Y = NH series, the former series therefore tends to have a higher activation energy than the latter for conversion of the keto form into the enol form. The transition structure in the Y = CH_2 series has the greatest resemblance to its keto form, but it lacks the polarizing property and the bond energy effect of the C=Y double bond and, consequently, it has the highest activation energy for "enolization".

In the 2-substituted series, the electron delocalization effect stabilizes the enol form more than it does the keto form; on the other hand, the bond energy effect (i.e., the difference in bond energies between the C=Y double bond in the keto form and the C=C double bond in the enol form) stabilizes the keto form. The tautomeric processes for the Y = CH_2 series have transition structures ($n_T < 0.5$) bearing the greatest resemblance to their keto structures and, additionally, lack the bond energy effect. This feature results in the highest activation energy in the three series of equilibria for conversion of the keto form into the enol form. As we see in Table 1, the values of n_T follow the trend with respect to Y of O > NH, and both are > 0.5; consequently, the transition structures for the Y = O series have more enol component and less keto component than those in which Y = NH. Since the bond energy effect, which favors the keto form, is more significant than the delocalization effect, which favors the enol form, the activation energies for the different equilibria increase in the sequence, with respect to Y, of NH < O < CH_2.

C.2. Effects of Substituents

The results obtained from calculations (Table 1) suggest that, in the 1-substituted series, all substituents lower the activation energies when Y = CH_2; in the cases in which Y = O or NH the substituent X = CH_3 or NH_2 lowers the activation energies, while X = OH or F raises them. On the other hand, in the 2-substituted series, except when X = F, all substituents lower the activation energy.

In the 1-substituted series, the keto forms for the Y = CH_2 series lack the lone pair of electrons in the functional group C=CH_2 to bond to the migrating H4 atom and instead use their π-electron densities. The π-electron-donating ability of substituents therefore has more influence than their σ-electron-accepting ability on the activation energy. As the transition structure in this tautomeric series is loosely bonded, electron-donating substituents tend to push π-electron density toward the Y3 end of the C1=Y3 double bond (i.e., the C3 atom). This feature increases the ability of the C3 atom to receive the incoming H4 atom and consequently stabilizes the transition structure. The π-electron-donating abilities of the substituents X, which increase in the order H < CH_3 < F < OH < NH_2, result in the activation energies of "enolization" for the Y = CH_2 series of tautomeric interconversions decreasing in the sequence H > CH_3 > F > OH > NH_2. In the tautomeric series in which Y = O or NH, electron-donating substituents such as NH_2 and CH_3 tend to increase the electron density on the non-hydrogen atom of Y in the functional group C=Y. This situation expedites the migration of the H4 atom and results in lower activation energies. Conversely, substitution with electron-withdrawing groups (OH and F) results in higher activation energies. The orders of increasing electron-donating (CH_3 < NH_2) and electron-withdrawing abilities (OH < F) account for the activation energies increasing, with respect to X, in the order NH_2 < CH_3 < H < OH < F.

In the 2-substituted series, the activation energies of "enolization" for the various functional groups in this series all decrease in the sequence, with respect to X, H > CH_3 > F > OH > NH_2. As noted above, each substituent has a greater impact on reducing the energy of the enol form than of the keto form and the transition structures all have ca. 50% enol content. Consequently, substituents that stabilize the enol form over the keto form also stabilize the transition structure and therefore lower the activation energy. As discussed earlier, the ability of the substituents to stabilize the enol form increases in the order H < CH_3 < F < OH < NH_2, which reflects the sequence of decreasing activation energies.

Conclusion

Among all of the six tautomeric series we have investigated, keto forms are thermodynamically more stable than enol forms, with the exceptions of the 1-substituted propene−propene (Y = CH_2) series, in which enol and keto forms are identical, and the 2-substituted propene−propene series, in which the enol forms are lower in energy than the keto forms.

The computed relative energy of an enol form with respect to its keto form increases with increasing electronegativity (Pauling scale) of the non-hydrogen atom in the functional group Y. A very good linear correlation exists between these values.

The influence of a functional group Y on the stabilities of the tautomers is exerted by its effect on bond energies to a greater degree than its effect on the dispersion of electron charge through resonance.

The effect of substituent X on the relative energy can be explained in terms of the changes in bond dissociation energies and dispersion of charge through resonance effects. The former, as explained by means of the isodesmic reaction, and the latter by NBO analysis, follow the same trends.

The NBO analyses suggest that the π-electron-donating and σ-electron-accepting influences of the substituents increase in the orders H < CH_3 < F < OH < NH_2 and H < CH_3 < NH_2 < OH < F, respectively. In the 1-substituted series, π-electron-donating substituents increase the relative energies by stabilizing the keto form over the enol form, except when Y = CH_2, in which case both forms are identical (E_r = 0). The opposite effect is true in the case of the 2-substituted series.

There is no linear correlation between the activation energies for tautomerism and the electronegativities of the

non-hydrogen atom in the functional group Y. In both the 1- and the 2-substituted series, the influence of the functional group Y increases the activation energy in the sequence $NH_2 < O < CH_2$, but the effect of the substituent X depends on its position of substitution. In the 2-substituted series, substitution by X lowers the activation energy. Conversely, in the 1-substituted series, the substituents lower the activation energy only when Y = CH_2; when Y = NH or O, the activation energy increases in the order $NH_2 < CH_3 < H < OH < F$.

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[29] The optimized geometric parameters calculated at the HF/6−31G**, MP2(full)/6−31G*, and B3LYP/6−31G** levels for all the examined structures are presented in Table S-1 in the supporting information (for Supporting Information see also the footnote on the first page of this article). The enol form structures of the 2-substituted series were calculated in their trans (*E*) forms.
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[33] See Table S-4 in the Supporting Information.
[34] The trend in the results computed at the different levels of theory is presented in Figure S-3 in the Supporting Information.
[35] The values of stabilization energy and the bond order of the C=C double bond are listed in Table S-5 in the supporting information. These data provide insight into the flow of electrons and hydrogen atoms, which migrate with a positive charge, and the relative energy of the enol form with respect to the keto form in the various tautomeric interconversions.
[36] See Table S-6 in the Supporting Information.
[37] See Figure S-4 in the Supporting Information.
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