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Testing the Validity of the Conventional Resonance Model for Protonated Carbonyl, Imine and Thiocarbonyl Compounds. An Ab Initio Valence Bond Study

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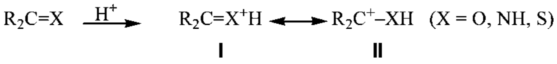
ABSTRACT

The conventional resonance model describes protonated carbonyls, imines, and thiocarbonyls by a superposition of two structures, one π polar-covalent and the other of carbenium type. The validity of this model is clearly supported by high level valence bond calculations, giving a 32% weight for the carbenium form in protonated carbonyl, 19% in protonated formamine and thioformaldehyde. The carbenium form is further stabilized by π-donating substituents. Solvation effects do not fundamentally change the gas-phase picture.

Protonated carbonyl, imines, and thiocarbonyl compounds are important intermediates in many acid-catalyzed reactions. In all of these ions, the positive charge of the heteroatom can delocalize into the neighboring carbon atom through a resonance interaction, as depicted in Scheme 1.

Scheme 1. Mesomeric Scheme for Protonated Carbonyl, Imines, and Thiocarbonyl Compounds



$$R_2C{=}X \xrightarrow{H^+} \underset{\mathbf{I}}{R_2C{=}X^+H} \longleftrightarrow \underset{\mathbf{II}}{R_2C^+{-}XH} \quad (X = O, NH, S)$$

For example, in the protonated carbonyl case (X = O), the carboxonium ion exhibits both oxonium (**I**) and carbenium (**II**) character, and analogous resonance structures are postulated for protonated imines and protonated thiocarbonyl compounds. It should be noted that the XH bond is quite polar, with the consequence that the positive charge mainly sits at the hydrogen, in line with computed electrostatic potential. Now, what is the amount of double bond character that is retained after protonation? In other words, what are the respective weights of **I** and **II**? This question has attracted the attention of experimentalists as well as theoreticians for several decades, especially in the carbonyl case. On the experimental side, ^{17}O NMR shifts have been used as indicators of carbon−oxygen π-bond order.[1,2] Such studies have generally led to the conclusion that a substantial double-

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bond character is retained in the carbonyl carbon−oxygen bond on protonation, although weakening of the carbonyl double bond is evident in some cases.[2,3] More quantitatively, in the case of acetone, Olah estimates that protonation induces a decrease of carbon−oxygen π bond order of about 40%, thus assuming weights of 60% and 40%, respectively, for **I** and **II**.[4]

On the theoretical side, several criteria have been used to test the validity of the resonating Scheme 1. Thus, since **II** displays a single C−X bond as opposed to a double bond in **I**, one expects an increase of the CX bond length upon protonation of the $R_2C{=}X$ molecule. Indeed, theoretical studies[5–7] show a modest, but significant bond lengthening upon protonation of carbonyl compounds (more than 0.05 Å for a series of ketones).[7] By contrast, bond lengthening was found to be much smaller, 0.004 Å and 0.011 Å, respectively, upon protonation of formaldimine ($R = R' = H$, $X = NH$) and thioformaldehyde ($R = R' = H$, $X = S$).

Another criterion that has been used to estimate the weights of **I** vs **II** is based on calculated net atomic charges. Several authors[5,7–9] have calculated the variations of net charges upon protonation of several carbonyl compounds using “Atom in Molecules” (AIM) theory,[10] and some of them compared the results to those arising from another definition of net charges, so-called “Hirshfeld”[11] (also called “Stockholder”) atomic partitioning.[8] While the two net charge definitions strongly disagree with each other as far as total atomic charges are concerned, consistent trends were obtained when considering π net charges alone, which are the only net charges to consider to settle a question of mesomerism in the π electronic system. Recall that the two electrons of the π system are shared by both carbon and oxygen in the unprotonated molecule and in the form **I**, while all of the π population is concentrated on the oxygen atom in **II**. Therefore, any participation of **II** in the protonated species should be characterized by an increase of the π electron population at oxygen and a concomitant decrease at carbon, relative to the unprotonated species. These are indeed the tendencies that emerge from net atomic charge calculations. From Hirshfeld population analysis, the π electron population increases by $+0.220$ e^- and decreases by -0.261 e^- at oxygen and carbon, respectively, upon protonation of formaldehyde ($R = R' = H$, $X = O$). Upon protonation of formaldimine ($R = R' = H$, $X = NH$), the increase at nitrogen and decrease at carbon amount to $+0.120$ $e^-$and -0.160 e^-, respectively. Thus, in both cases, a significant participation of the resonance structure **II** is evidenced for the protonated species, and more so for formaldehyde than for formaldimine. It is noteworthy that AIM population analysis reveals electron transfers of the same orders of magnitude upon protonation[8] but larger in formaldimine than in formaldehyde, at variance with Hirshfeld net charge definition.

As can be seen, the various criteria that have been used in theoretical studies to evaluate the validity of the resonating Scheme 1 leave some open questions: What are the real weights of the resonance structures? How important is the influence of π-donating substituents? What is the influence of a polar solvent? The most simple and straightforward way to answer these questions is to perform a direct calculation of the weights of the resonance structures that are involved in the protonated carbonyl, imine and thiocarbonyl compounds, and this can be achieved by use of valence bond (VB) theory which, in its modern forms,[12–14] is now able to quantify chemical paradigms in a reliable way.

In VB theory, a many-electron wave function is expressed in terms of VB functions Φ_K

$$\Psi = \sum_K C_K \Phi_K \qquad (1)$$

where each Φ_K corresponds to a traditional VB structure. In the present work, the VB wave functions are calculated by the “breathing-orbital valence bond method” (BOVB),[14] a method that has been extensively tested for its reliability.[14c] Only the π system is treated at the VB level, while the other electrons are in doubly occupied molecular orbitals. However, all orbitals are optimized, so that the influence of the C-R σ bonds and σ lone pairs on the π system is accounted for. As is usually done, the importance of each VB structures Φ_K is characterized by its “weights” W_K, which is extracted from the coefficients (see the Supporting Information for the definition of the weights and for a brief description of the BOVB method).

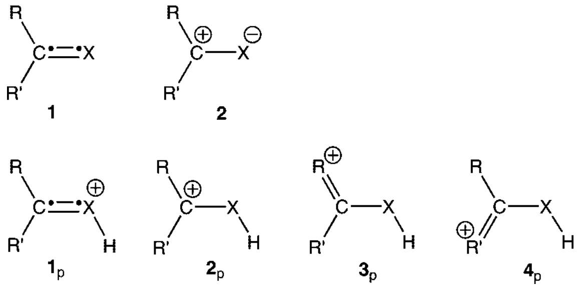

Figure 1. Valence bond structures for the unprotonated species (**1**−**2**) and for the protonated species (**1P**−**4P**).

The VB structures that are considered in the present work are displayed in Figure 1. At variance with previous VB

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computations,[15] the π atomic orbitals (AO) that are used to define the VB structures are strictly localized on a single atom (C or X) or fragment (R or R′), unless otherwise specified. This way, the distribution of electrons in the π space is very clear. For example, VB structures **1** and $\mathbf{1_P}$ that display a purely covalent π bond (noted •−•), have one π electron on C and another on X. VB structures having inverse polarity, of the type $RR'C^{-}{-}O^{+}$ or $RR'C^{-}{-}O^{2+}H$, are discarded for the sake of simplicity. All VB calculations were performed with the XMVB ab initio valence bond program of the Xiamen group.[16]

Table 1. Weigths of VB Structures for Formaldehyde, Formaldimine, Thioformaldehyde, and Their Protonated Species

	Carbonyl, imine, thiocarbonyl		Protonated species		
	$H_2C\overset{\cdots}{-}X$ **1**	$H_2C^{+}{-}X^{-}$ **2**	$H_2C\overset{\cdots}{-}X^{+}H$ $\mathbf{1_P}$	$H_2C^{+}{-}XH$ $\mathbf{2_P}$	$H_2C{=}X^{+}H/H_2C^{+}{-}XH$ **I / II**
O	68.0	32.0	48.8	51.2	0.718 / 0.282
NH	73.4	26.6	59.3	40.7	0.808 / 0.192
S	75.7	24.3	61.5	38.5	0.812 / 0.188

In a first step, let us consider the parent compounds $H_2C{=}X$ and their protonated derivatives, $[H_2CXH]^{+}$. The calculated weights for the unprotonated species are displayed in Table 1, columns 1 and 2. It is seen that the π bond of $H_2C{=}X$ involves a major purely covalent component **1** combined with a minor ionic component **2**, and the ratio between these two components characterize the polarity of the familiar polar-covalent bond $C{=}X$. Thus, the π bond of formaldehyde is more polar (covalent/ionic ratio of 68:32) than that of imine, itself slightly more polar than thioformaldehyde, owing to electronegativity decreasing in the series O, N, S.

The same analysis performed on the protonated species (structures $\mathbf{1_P}$ and $\mathbf{2_P}$, columns 3 and 4) shows that protonation affects the CX π bond in a significant way, diminishing the weight of the covalent component $\mathbf{1_P}$ and inceasing that of the ionic component $\mathbf{2_P}$, which can be interpreted as a participation of **II** in the resonating Scheme 1. More quantitatively, let us define structure **I** of the protonated species as displaying a polar π bond identical to that of the unprotonated species $H_2C{=}X$ (e.g., 68% covalent and 32% ionic in the $H_2C{=}O$ case). Thus, the weight of **I** in column 5 of Table 1, W(**I**), measures that part in the π bond of $[H_2CXH]^{+}$ that is unchanged relative to the unprotonated species $H_2C{=}X$. This is readily estimated through eq 2

$$W(\mathbf{I}) = W(\mathbf{1p})/W(\mathbf{1}) \qquad (2)$$

where $W(\mathbf{I})$, $W(\mathbf{1_P})$, and $W(\mathbf{1})$ refer to the weights of structures **I**, **1**, and $\mathbf{1_P}$, respectively. With this definition, the contribution of **II** to the resonating Scheme 1 is simply the complement of $W(\mathbf{I})$ to unity. From this analysis and the weights displayed in column 5 of Table 1, it appears that the π bond in protonated formaldehyde can be viewed as a combination of 72% of polar-covalent bond, unchanged relative to formaldehyde, and 28% of carbenium structure. Protonated imine and thioformaldehyde also exhibit a significant, albeit smaller, contribution of the ionic resonance structure **II** (19%). *Thus, the validity of the classical resonating Scheme 1 is clearly supported by the VB calculations*.

As a general rule, π-donating substituents are known to stabilize carbenium structures, and should therefore tip the **I**/**II** balance in Scheme 1 in the sense of increasing the weight of **II** or, equivalently, to decrease the weight of structure $\mathbf{1_P}$ if one prefers to think in terms of purely covalent and purely ionic structures. The carbenium stabilization may arise from two distinct effects: (i) a simple donating inductive effect resulting from the presence of the substituent's π-electron density in the vicinity of the C^{+} center; this effect should manifest itself by an increase in weight of structure $\mathbf{2_P}$. (ii) A hyperconjugative effect, which in mesomeric language corresponds to structures $\mathbf{3_P}$ and $\mathbf{4_P}$ entering into play.[17] As we find it important to disinguish between inductive and hyperconjugation effects for substituted compounds, we are going to abandon the quantitative reasoning in terms of **I**/**II** in what follows, and we will reason in terms of purely covalent or ionic structures $\mathbf{1_P}-\mathbf{4_P}$. In this framework, the overall stabilization of the carbenium form **II** will be qualitatively characterized by the added weights of structures $\mathbf{2_P}$, $\mathbf{3_P}$, and $\mathbf{4_P}$, relative to those of the parent species.

Table 2. Weights of VB Structures $\mathbf{1_P}-\mathbf{4_P}$ for Protonated Carbonyl, Imine, and Thiocarbonyl Compounds

X, R, R'	$RR'C\overset{\cdots}{-}X^{+}H$ $\mathbf{1_P}$	$RR'C^{+}{-}XH$ $\mathbf{2_P}$	$R^{+}{=}CR'{-}XH$ $\mathbf{3_P}$	$R'^{+}{=}CR{-}XH$ $\mathbf{4_P}$	$(RR'C)^{+}{-}XH$ $\mathbf{2_P+3_P+4_P}$
O,H,H	48.8	51.2			51.2
O,CH_3,H	40.8	51.5	7.7		59.2
O,CH_3,CH_3	35.2	51.9	6.1	6.8	64.8
NH,H,H	59.3	40.7			40.7
NH,CH_3,H	52.5	42.9	4.6		47.5
NH,CH_3,CH_3	46.7	44.8	4.3	4.3	53.4
S,H,H	61.5	38.5			38.5
S,CH_3,H	50.1	43.1	6.8		49.9
S,CH_3,CH_3	40.6	46.8	6.3	6.3	59.4

Taking methyl as a typical π-donating substituent, the effects of mono and disubstitutions are analyzed in Table 2. Let us consider monosubstitutions first. It is immediately apparent that substitution by a methyl group has the effect of decreasing the weight of the covalent structure $\mathbf{1_P}$ (or, equivalently, increasing that of $\mathbf{2_P}$, $\mathbf{3_P}$, and $\mathbf{4_P}$) in a significant way: from 48.8% to 40.8% in the carbonyl case, from 59.3% to 52.5% in the imine case, and from 61.5% to 50.1% in the

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thiocarbonyl case. If one decomposes the carbenium-stabilizing effect, it is seen that substitution induces a modest increase of the weights of structure $\mathbf{2_P}$, except perhaps in the thiocarbonyl case, showing that the inductive effect is rather small, while hyperconjugative effects are dominant in all cases. Be it as it may, it is clear from these results that methyl substitution increases the weight of the carbenium form in Scheme 1, especially in disubstituted compounds, in which substituent effects appear to be practically additive.

Table 3. Weights of VB Structures $\mathbf{1_P}-\mathbf{3_P}$ for Protonated Carbonyl Compounds

R	$RHC{=}O^{+}H$ $\mathbf{1_P}$	$RHC^{+}-OH$ $\mathbf{2_P}$	$R^{+}{=}CH-OH$ $\mathbf{3_P}$	$(RHC)^{+}-OH$ $\mathbf{2_P + 3_P}$
H	48.8	51.2		51.2
CH_3	40.8	51.5	7.7	59.2
SiH_3	46.0	52.1	1.9	54.0
OCH_3	26.4	43.0	30.6	73.6
SCH_3	28.8	40.5	30.7	71.2
NH_2	21.1	39.8	39.1	78.9
Cl	37.7	44.6	17.7	62.3

It is interesting to use the VB analysis to appreciate the π-donating ability of different substituents. To this aim, Table 3 displays the weights of structures $\mathbf{1_P}$, $\mathbf{2_P}$, and $\mathbf{3_P}$ for a series of protonated monosubstituted carbonyl compounds. Judging from the substituent effect on the weights of $(RHC)^{+}-OH$ ($\mathbf{2_P} + \mathbf{3_P}$, column 4), it is seen that silyl is a less efficient π-donating substituent than methyl. On the other hand, all the other substituents that are investigated here are more π-donating than methyl, in the order $NH_2 > OCH_3 > SCH_3 > Cl > CH_3$. In all these cases, the hyperconjugative effect, as can be judged by the weight of $\mathbf{3_P}$, is far more important than the π-inductive effect, the latter being characterized by the increase of the weight of $\mathbf{2_P}$ relative to the parent compound, R = H).

These results are complementary to a recent VB study investigating the energetic stabilization due to π-donating effects in different resonating systems, including substituted carbenium compounds.[18] This latter study, using a different family of valence bond wave function, based on Lewis structures,[19] and the resonance energy criterion rather than calculated weights, also concludes to the validity of the resonance model for carbonyl and protonated carbonyl compounds.

Since acid-catalyzed reactions occur, by necessity, in solvated phase, it is important to make sure that the above results, that are *stricto sensu* only valid in the gas phase, could not be affected by solvation effects. A simple way to check this is to use the fact that any variation of the **I**/**II** ratio, in eq 2, is directly related to a variation of the net π charge of the atom X. Thus, an increase (decrease) of the π electron population at atom X, under the effect of solvation, would indicate an increase (decrease) of the weight of **II** relative to **I** (or $\mathbf{2_P} + \mathbf{3_P} + \mathbf{4_P}$ relative to $\mathbf{1_P}$). This can be checked by any standard computational software (not necessarily VB), provided it is equipped with a solvation model, like the polarized continuum method (PCM)[20] that is implemented in the Gaussian 03 package of programs.[21] In accord, we recalculated all the protonated species investigated above at the B3LYP density functional level, with and without the PCM option, in order to get the π electron populations in the gas phase and in water phase, respectively. As a result, the B3LYP calculations (see the table in the Supporting Information) show rather similar net π charges at the X atom from the gas phase to water phase, with maximum variations of 0.02 e^{-}, 0.05 e^{-}, and 0.01 e^{-} in the carbonyl, imine and thiocarbonyl cases, respectively, thus demonstrating the absence of significant solvent effects on the VB weights. This relative unimportance of solvent effects can be explained by the fact that both **I** and **II** are ionic structures, with no charge separation, so that solvation may stabilize both of them to nearly the same extent.

To conclude and summarize, the above valence bond calculations show that the traditional resonance model (Scheme 1) for the protonated carbonyls, imines, and thiocarbonyls is well founded. In agreement with this model, it is found that the electronic structures of these protonated species is a resonating combination of **I**, displaying a polar π bond analogous to that of the unprotonated compound, and **II**, displaying an additional component of pure carbenium character. The participation of **II** in the resonating scheme amounts to ca. 19% in formaldimine and thioformaldehyde, and reaches 32% in formaldehyde. The carbenium form is further stabilized by π-donating substituents, whose effects are additive, and in that case the hyperconjugative effects are important, as shown by the weights of the corresponding structures in VB language. Lastly, solvation by a polar solvent like water does not fundamentally change the gas-phase picture. It is rewarding that part of the present calculations, which by nature are directly connected to the weights of the various resonance structures, confirm the early estimations of Olah based on experimental ^{17}O chemical shifts.

Supporting Information Available: Detailed description of the theoretical methods, VB orbitals, and B3LYP net charges in gas phase vs water phase. This material is available free of charge via the Internet at http://pubs.acs.org.

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