JOC The Journal of Organic Chemistry

Article

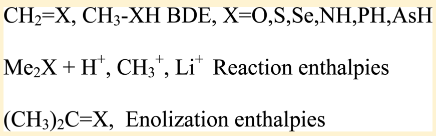
pubs.acs.org/joc

Calculations for the Properties and Reactions of the NH, PH, and AsH Counterparts of Dimethyl Ether and Acetone

Kenneth B. Wiberg*

Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107, United States

Supporting Information


CH_2=X, CH_3-XH BDE, X=O,S,Se,NH,PH,AsH

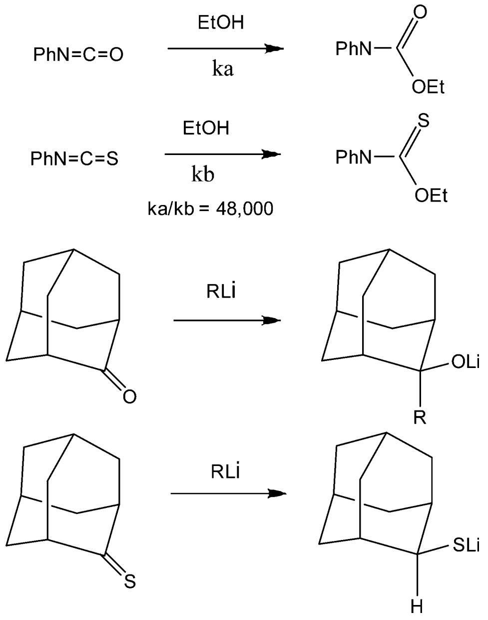
$Me_2X + H^+$, CH_3^+, Li^+ Reaction enthalpies

$(CH_3)_2C$=X, Enolization enthalpies

ABSTRACT: The properties and reactions of compounds in which the O of dimethyl ether or acetone has been replaced by NH, PH, or AsH have been studied computationally using CBS-QB3, CBS-APNO, G4, and W1BD. The properties include the bond dissociation energies and ionization potentials, and the reactions include those with with protons, methyl cations, and lithium cations. The effect on keto−enol equilibria also was examined. In all cases there was good agreement with the available experimental data. The agreement between these methods suggests that the least computationally costly model (CBS-QB3) should be of general use in studying organic compounds. The double-bond dissociation enthalpies of $CH_2{=}XH_n$ were linearly related to those of the corresponding $CH_3{-}XH_{n+1}$ single bonds with a slope of 2.5. With the exception of C−C, the order corresponded to the electronegativity of X, suggesting that the differences are largely determined by internal Coulombic interactions. The differences in the electronegativities of the heteroatoms are largely responsible for the differences in the properties and reactions. Oxygen has a significantly higher electronegativity than the others, and as a result, the oxygen-substituted compounds are often different than the others.

1. INTRODUCTION

In order to better understand the effect of heteroatoms on the properties of organic compounds, we have carried out computational studies of the effect of replacing the O of dimethyl ether or acetone with S or Se.[1] In addition, our experimental studies showed that in the reaction with ethanol, phenyl isocyanate is 48 000 times more reactive than phenyl isothiocyanate[2] and that the reaction of *n*-butyllithium with 2-adamantanone gives the tertiary alcohol whereas the reaction with 2-adamantathione gives mainly the reduction product, adamantanethiol.[3] A computational study of these reactions has been reported, and the calculations were in very good accord with the available experimental data.[1,3]



We have now continued this study by replacing O with NH, PH, or AsH in order to gain a better understanding of the effect of moving one step across the periodic table. There are relatively few experimental data for these compounds, but the good agreement found for S and Se substitution makes it likely that the present computational results will be useful in understanding trends as one moves about the periodic table. In view of the sparse experimental data, we made use of four of the common and well-tested model chemistries, namely, CBS-QB3,[4] G4,[5] CBS-APNO,[6] and W1BD.[7,8] Agreement among the methods would give confidence in the calculated results when experimental data are absent.

2. RESULTS AND DISCUSSION

a. Bond Dissociation Enthalpies. The strengths of double bonds such as $CH_2{=}X$ have been of interest to chemists for many years and are probably best represented by the bond dissociation enthalpy (BDE, ΔH_{298}). In a few cases, experimental values for a parent molecule and the two fragments formed by bond dissociation have independently been measured, thereby providing an experimental value for the dissociation enthalpy.[9] However, in most cases this is a quantity that cannot be measured directly,[9] and it is usually obtained via calculations such as from the difference in enthalpy at 298 K between the parent compound and those of triplet methylene and the triplet state of the atom or group formed in the dissociation, i.e., $H_2C{=}X \rightarrow {}^3CH_2{:} + {}^3X{:}$. Although there have

Received: August 10, 2014
Published: October 30, 2014

dx.doi.org/10.1021/jo501849a | *J. Org. Chem.* 2014, 79, 10849−10854

been many such calculations,[10−15] it seemed desirable to repeat them using more recent theoretical methods. We used several different compound methods and obtained the results shown in Table 1. The CBS-QB3 and CBS-APNO methods are complete basis set procedures developed by Petersson and co-workers;[4,6] G4 is the more recent of the Gaussian series[5] initially developed by Pople, and W1BD was developed by Martin and co-workers.[7,8] Of these, CBS-QB3 is the least computationally expensive, G4 and CBS-APNO are roughly comparable in CPU time and accuracy, and W1BD is the most computationally intensive and generally gives very good agreement with experiments. Only CBS-QB3 and G4 were able to accommodate all of the atoms in this study. CBS-APNO is limited to first-row elements, and W1BD is currently limited to first- and second-row elements. In Table 1 we have included the results for $CH_2{=}S$ and $CH_2{=}Se$[1] to allow a comparison. The ROCBS-QB3 variant was used in order to minimize the effect of spin contamination in the triplet species.[16] There will be spin−orbit effects for the third-row elements,[17] but in the absence of specific data it was assumed that these effects approximately canceled between reactants and products.

Table 1. Calculated C=X Bond Dissociation Enthalpies, ΔH_{298} (in kcal/mol)

compound	ROCBS-QB3	G4	CBS-APNO	W1BD	observed[1]
$H_2C{=}CH_2$	175.6	173.9	175.3	174.7	174.1 ± 0.3
$H_2C{=}O$	181.0	179.4	179.7	179.3	179.0 ± 0.4
$H_2C{=}S$	133.2	132.2		131.9	132.0 ± 2.0
$H_2C{=}Se$	112.2	111.4			
$H_2C{=}NH$	158.9	157.8	158.4	158.1	
$H_2C{=}PH$	123.2	121.9		121.8	
$H_2C{=}AsH$	107.2	106.6			

It can be seen that all of the methods give essentially the same BDE values, which agree well with the available experimental data. The W1BD method gives the most satisfactory result, but at a computational cost much greater than for the other methods. The largest BDE is found with C=O, which is probably strengthened with respect to C=C by its $C^{+}{-}O^{-}$ polar character. The BDE of $H_2C{=}NH$ is less than that of $H_2C{=}O$ by 21 kcal/mol, which is at least in part due to the less polar character of a C−N bond. The differences for the other pairs of compounds are smaller and about 5−10 kcal/mol.

For these compounds, the BDE has two parts: the σ and π components. There has been much interest in obtaining the separate energies for the two components, but none of them are entirely satisfactory.[10−15] In order to have some reference for considering this question, Table 2 gives the calculated single-bond dissociation enthalpies. They are of interest in themselves.

In this case also, all of the calculations for a given compound give essentially the same BDE, which also agrees with the experimental result. The BDE for $MeNH_2$ is significantly smaller than that for MeOH, which in turn is smaller than that for MeF (101.4 kcal/mol by W1BD). As we found in a study of the halomethanes,[18] this is the order expected on the basis of the electronegativities[19] and the resulting changes in charges. Internal charge separation leads to internal Columbic attraction, which results in an increase in bond strength.[20] The Hirshfeld charges[21] calculated at the B3LYP/aug-cc-pVTZ level are −0.143*e* at F in MeF, −0.089*e* at OH in MeOH, and −0.048*e* at NH_2 in $MeNH_2$. These charges account for much of the difference in the BDEs. Correspondingly, the C−X bond length decreases in going from $MeNH_2$ (1.4636 Å) to MeOH (1.4208 Å) to MeF (1.3864 Å) The one discordant feature is that ethane, with no electronegativity difference between the atoms, has a BDE between that of MeOH and $MeNH_2$. This may be a result of having no lone pairs that could lead to repulsive interactions with the methyl groups.

Table 2. Calculated Single-Bond Dissociation Enthalpies (in kcal/mol)

compound	ROCBS-QB3	G4	CBS-APNO	W1BD	obs[9]
$CH_3{-}CH_3$	89.2	89.0	90.7	90.3	90.1 ± 0.1
$CH_3{-}OH$	92.2	91.3	92.5	92.3	92.1 ± 0.1
$CH_3{-}SH$	74.2	74.0		74.8	
$CH_3{-}SeH$	65.3	65.8			
$CH_3{-}NH_2$	84.3	83.7	85.0	84.8	85.2 ± 0.3
$CH_3{-}PH_2$	71.0	71.0		71.6	
$CH_3{-}AsH_2$	63.9	63.2			

The double-bond and single-bond BDEs are well-correlated, as can be seen in Figure 1. The C=X BDE changes about 2.5 times as rapidly as the C−X value. The observation of a linear relationship suggests that the changes in double-bond dissociation energy also result in large part from internal Coulombic interactions. For example, in formaldehyde the Hirshfeld charge[21] at O is −0.234*e*, whereas that at NH in formaldimine is only −0.103*e*. A part of the larger change in double-bond BDEs may also be due to their shorter bond lengths, which can lead to larger internal Coulombic interactions.

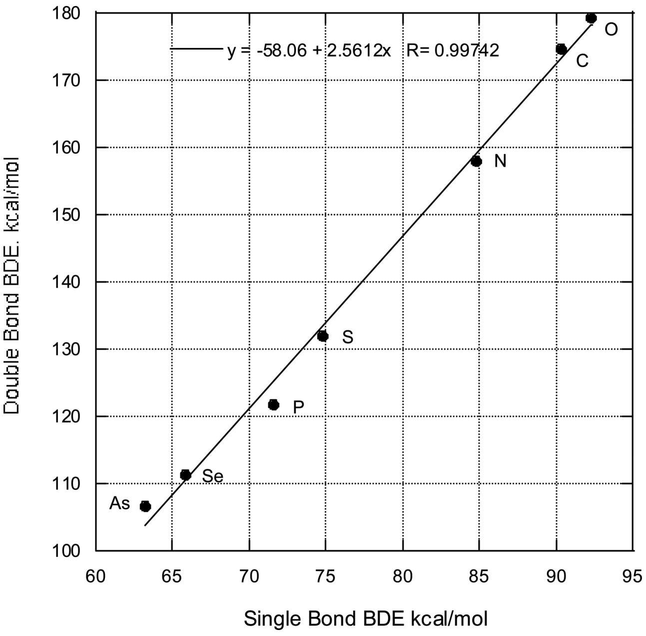


Figure 1. Relationship between the double- and single-bond dissociation energies. W1BD energies were used for all except Se and As, where G4 was used.

There have been numerous attempts to estimate the π component of the double-bond BDE, D_{π}.[10−15] One cannot simply subtract the single-bond energy from that of the double bond because of the different numbers of hydrogens. Schmidt, Truong, and Gordon[22] suggested that a correction could be made via the following reactions:

$$\begin{array}{ll} H_3C{-}OH \rightarrow H_2C{=}O + H_2 & \Delta H_{\mathrm{hydrog}} \\ H^\bullet + H_2C^\bullet{-}OH \rightarrow H_3C{-}OH & -D(CH) \\ H^\bullet + H_2C^\bullet{-}O^\bullet \rightarrow H_2C^\bullet{-}OH & -D(OH) \\ H_2 \rightarrow 2H^\bullet & D(H_2) \\ H_2C^\bullet{-}O^\bullet \rightarrow H_2C{=}O & D_\pi \end{array}$$

From these reactions, it follows that

$$D_\pi = D(CH) + D(OH) - \Delta H_{\mathrm{hydrog}} - D(H_2)$$

Here $D(OH)$ was taken as the value for $CH_3O{-}H$ since it cannot be calculated directly. The several terms were calculated using G4, giving the π-bond dissociation energies listed in Table 3. This method was also used with the other heteroatoms. The values of the terms may be found in the Supporting Information. Table 3 also includes the π energies estimated by calculating the barrier to rotation about the double bond where this method is applicable.[22]

Table 3. Calculated π-Bond Dissociation Energies (in kcal/mol)

compound	calculated	bond rotation
$CH_2{=}CH_2$	64.8	65.4
$CH_2{=}O$	74.8	
$CH_2{=}S$	51.0	
$CH_2{=}Se$	41.0	
$CH_2{=}NH$	61.9	63.3
$CH_2{=}PH$	42.4	43.1
$CH_2{=}AsH$	41.9	

There is remarkably good agreement between the π-bond dissociation energies calculated via the two methods. However, this is probably due to some cancellation of errors. In the above reactions, the value of $D(OH)$ for $CH_2O{-}H$ was assumed to be the same as that for $CH_3O{-}H$. It would be surprising if the energies of these two O−H bonds were the same. In addition, a double bond has a shorter length than a single bond, and this difference in bond length was not taken into account. In the π-bond rotation calculations, it is possible that in the transition state there is an interaction between one electron in a p orbital and the bonds on the adjacent atom. The bond length problem also applies.

b. Ionization Potentials. The first ionization potential (IP) reflects how tightly the electrons are bound. It is known that the IP of dimethyl sulfide is significantly smaller than that of dimethyl ether[23] and that dimethyl ether and acetone have similar ionization potentials.[23] It would be interesting to see how the corresponding N, P, and Se compounds are related. In our previous study, CBS-QB3 was found to reproduce the experimental values,[1] and as a result, this level was also used here. The other model chemistries also were used in order to compare them. Methyl substitution is known to have significant effects on the basicity and ionization potentials of amines, and therefore, this was the focus of the initial study. The data are given in Table 4, which includes values for the related O, S, and Se compounds for comparison. The experimental data were taken from the NIST Chemistry Webbook.[23]

Table 4. Effect of Methyl Substitution on the Ionization Potentials (in eV)

compound	CBS-QB3	G4	CBS-APNO	W1BD	obs[23]
NH_3	10.17	10.16	10.18	10.18	10.07 ± 0.02
$MeNH_2$	9.18	9.05	9.06	9.06	8.9 ± 0.1
Me_2NH	8.36	8.32	8.30	8.33	8.24 ± 0.08
Me_3N	7.88	7.88	7.85	7.86	7.85 ± 0.05
PH_3	9.86	9.91		9.87	9.87 ± 0.01
$MePH_2$	9.00	9.04		8.99	9.12 ± 0.07
Me_2PH	8.37	8.38		8.37	8.47 ± 0.07
Me_3P	7.89	7.88		7.92	8.12
AsH_3	9.82	9.80			9.89
$MeAsH_2$	8.34	9.06			8.5
Me_2AsH	8.55	8.49			
Me_3As	8.10	8.06			8.2
H_2O	12.64	12.59	12.61	12.62	12.62 ± 0.002
MeOH	10.92	10.87	10.89	10.87	10.84 ± 0.01
Me_2O	10.03	9.98	10.02	10.00	10.03 ± 0.03
H_2S	10.43	10.45			10.46 ± 0.01
MeSH	9.47	9.45			9.44 ± 0.01
Me_2S	8.69	8.85			8.69 ± 0.01
H_2Se	9.95	9.90			9.89 ± 0.01
MeSeH	9.14	9.08			
Me_2Se	8.43	8.38			8.38 ± 0.02

In all cases where there is an estimate of the uncertainty, there is good agreement between the calculations and experiments. There are considerable differences in ionization potential in going from the O derivatives to the S and Se derivatives, whereas with the N, P, and As series the differences are quite small, as shown in Figure 2. The slopes of the lines in Figure 2 are about the same, with the exception of that for the O derivatives.

The large difference between water and its analogues and the other compounds suggests that there may be a considerable

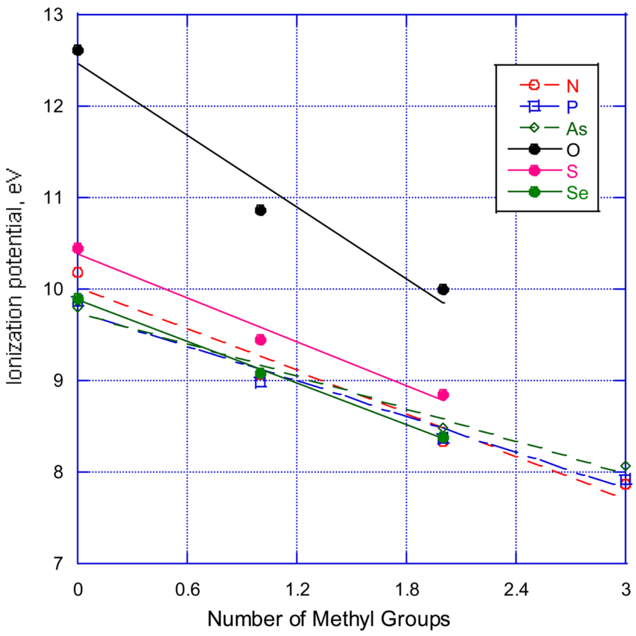


Figure 2. Effect of methyl substitution on the ionization potentials of H_2O, H_2S, H_2Se, NH_3, PH_3, and AsH_3. The first three compounds give significant differences, but with the latter three the ionization potentials are quite similar and about the same as for the R_2Se series.

difference in charge distribution among the compounds. This possibility was explored using the Hirshfeld charges,[21] which are derived by a comparison between the calculated charge distribution in the real molecule and that for a promolecule having neutral, spherically symmetrical proatoms at the coordinates of the real molecule. The charges thus obtained using UQCISD/6-311++G(2df,p) wave functions (corresponding to one of the later calculations in CBS-APNO) are given in Table 5. CBS-APNO geometries (QCISD/6-311g(d,p)) were used for the first-row cases, and G4 geometries (B3LYP/GTBas3) were used for the others.

Table 5. Calculated Hirshfeld Charges for Radical Cations (in *e*)

compound	atom/group	X = N	X = P	X = As
XH_3	X	0.230	0.716	0.683
	H	0.257	0.095	0.106
$MeXH_2$	Me	0.383	0.246	0.249
	X	0.163	0.583	0.571
	H	0.227	0.086	0.090
Me_2XH	Me	0.325	0.207	0.211
	X	0.143	0.518	0.509
	H	0.207	0.068	0.072
Me_3X	Me	0.287	0.176	0.180
	X	0.140	0.473	0.459
compound	**atom/group**	**X = O**	**X = S**	**X = Se**
XH_2	X	0.315	0.642	0.720
	H	0.343	0.179	0.140
MeXH	Me	0.579	0.318	0.289
	X	0.144	0.527	0.581
	H	0.287	0.158	0.130
Me_2X	Me	0.430	0.274	0.251
	X	0.141	0.453	0.497

With compounds having second- or third-row elements, most of the positive charge is borne by the heteroatom. However, in the compounds containing N or O, most of it is borne by the substituents. This is not surprising, since as a result of the higher electronegativity of N, most of the positive charge in ammonium ion is found at the hydrogens (N, 0.0621*e*; H, 0.2345*e*), and the same is found with hydronium ion (O, 0.051*e*; H, 0.3160*e*). Hydrogens, as a result of their small nuclear charge, are able to accept either positive or negative charges from the attached atoms.[24] The added electrostatic benefit of spreading the charge over as large a volume as possible also contributes, since the hydrogens generally lie on the periphery of a given molecule.

Methyl substitution leads to a decrease in charge at X and a reduction in the ionization potential. The effect is largest with X = O since O has the highest electronegativity and can best benefit from methyl stabilization. There is a corresponding larger effect of methyl substitution on the spin density at O in the radical cations (Table 6). The unsubstituted compounds have high spin densities at the heteroatom. Methyl substitution reduces the spin density, and this effect is seen mainly with N and O.

c. Gas-Phase Reactions with Protons, Methyl Cations, and Lithium Ions. The energy change in the reactions of these compounds with protons is known as the proton affinity (PA = $-\Delta H_{\text{reaction}}$), that with methyl cation is known as the methyl affinity, and that with lithium cation is known as the lithium affinity. In the case of the O, S, and Se compounds that we studied previously, there was an increase in $\Delta H_{\text{reaction}}$ for protonation in going down the periodic table, but the order was reversed for the reaction with lithium cation.[1] Evidence was presented that the orders were related to the degree of charge transfer in the reactions, which is large with protons and small with lithium cations. In order to see whether this is also the case in the present series, we carried out computational studies that are summarized in Table 7. Only CBS-QB3 and G4 were available for all of the elements, and they gave similar values. The G4 relative enthalpies of reaction are given in Table 7. Other data are available in the Supporting Information. The effect of methyl substitution on the protonation enthalpy is shown in Figure 3. An earlier computational study by Howard, Foreman, and Edwards included the protonation of the parent amines and their trimethyl derivatives,[25] and Martin and Lee reported a high-level calculation for the proton affinity of ammonia.[26]

Table 6. Calculated Spin Densities at the Radical Centers of Radical Cations

compound	X = N	X = P	X = As
XH_3	0.8787	0.8977	0.8937
$MeXH_2$	0.7552	0.8356	0.8400
Me_2XH	0.7074	0.7889	0.7976
Me_3X	0.6896	0.7528	0.7622
compound	**X = O**	**X = S**	**X = Se**
XH_2	0.9502	0.9643	0.9746
MeXH	0.6325	0.8850	0.9270
Me_2X	0.6777	0.8428	0.8934

There is almost a linear relationship between the enthalpy of protonation of the phosphene and arsene derivatives and the number of methyl substituents, There is a similar effect in going from NH_3 to Me_2NH, but as observed experimentally, the third methyl substitution has little effect.[27] This is probably due to the relatively short $N{-}CH_3$ bond lengths.[28] As a result, in Me_3NH^+, the methyl groups, which bear most of the positive charge, are forced to be nearer to each other, leading to significant Me···Me repulsion. From Figure 3, this effect, which is commonly called B-strain,[26] may be estimated to be about 10 kcal/mol. However, this explanation has not been universally accepted.[29]

The protonation energies are much larger than those for the reaction with methyl cation, and the latter are much larger than those for the reaction with lithium cation. This is probably related to the amount of charge transfer to the cationic reagent. This was confirmed by calculating the Hirshfeld charges, and the values are given in parentheses in Table 7. With protons, the charge transfer is smallest with ammonia and increases with methyl substitution and with the compounds having the less electronegative P and As atoms. The same trend was found for the reactions with methyl cation. However, the reactions with Li^+ show relatively small changes in reaction energy and charge transfer.

d. Acetone Analogues. The previous sections were concerned with water analogues. The acetone analogues were also studied, and the basic computational data (which were obtained using G4) are summarized in Table 8. A comparison with Table 7 shows that the reactions of Me_2NH have enthalpies close to those for the reactions of $Me_2C{=}NH$, as was also found in a comparison of Me_2O and $Me_2C{=}O$.[1] The reaction enthalpies of $Me_2C{=}PH$ and $Me_2C{=}AsH$ increase with methyl substitution more rapidly than those of Me_2PH and Me_2AsH.

Table 7. G4-Calculated Enthalpies of Reaction with a Proton, a Methyl Cation, and a Lithium Cation (in kcal/mol)

compound	H^+ calcd[a]	H^+ obs[23]	Me^+ calcd[b]	Li^+ calcd[c]
NH_3	−204.4 (0.765)	−204.0	−101.7 (0.685)	−38.5 (0.248)
$MeNH_2$	−212.3 (0.786)	−214.9	−116.6 (0.717)	−40.3 (0.275)
Me_2NH	−222.6 (0.808)	−222.2	−124.4 (0.743)	−40.8 (0.296)
Me_3N	−227.2 (0.816)	−226.8	−128.8 (0.764)	−40.7 (0.312)
PH_3	−186.7 (0.913)	−188.8	−105.4 (0.793)	−24.3 (0.297)
$MePH_2$	−204.0 (0.935)	−203.5	−121.5 (0.828)	−30.3 (0.318)
Me_2PH	−217.6 (0.925)	−218.0	−134.4 (0.856)	−34.8 (0.336)
Me_3P	−228.2 (0.966)	−229.2	−144.4 (0.880)	−38.3 (0.352)
AsH_3	−180.0 (0.898)	−178.8	−96.0 (0.816)	−22.4 (0.278)
$MeAsH_2$	−194.6 (0.918)		−109.5 (0.935)	−27.8 (0.298)
Me_2AsH	−206.2 (0.935)		−120.5 (0.840)	−31.8 (0.313)
Me_3As	−215.0 (0.948)	−214.5	−129.0 (0.863)	−34.6 (0.328)

[a]Values in parentheses are changes in Hirshfeld charge at H^+ when it reacts with a compound. [b]Values in parentheses are changes in Hirshfeld charge on

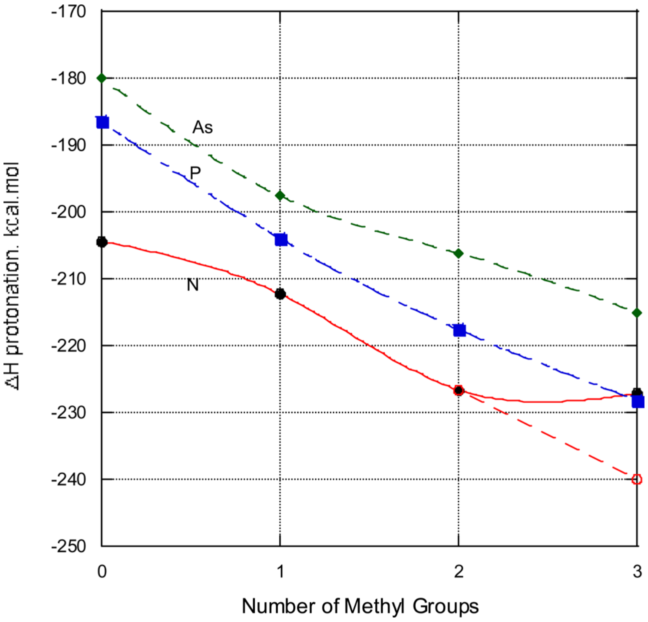


Figure 3. Effect of methyl substitution on the enthalpy of protonation. The curve for the amines was approximately extrapolated in accord with the three methyl group results for the other compounds.

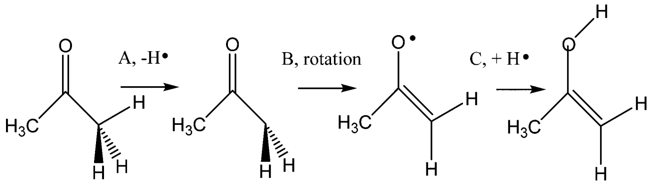
Table 8. G4-Calculated Ionization Potentials (in eV) and Reaction Energies (in kcal/mol) for Acetone Analogues

compound	IP	H^+ reaction	CH_3^+ reaction	Li^+ reaction
$Me_2C{=}NH$	9.11	−225.0	−124.9	−47.7
$Me_2C{=}PH$	8.94	−194.7	−109.5	−30.2
$Me_2C{=}AsH$	8.69	−186.2	−99.9	−28.3
$Me_2C{=}NMe$	8.40	−228.4	−129.8	−48.4
$Me_2C{=}PMe$	8.55	−206.7	−120.6	−34.2
$Me_2C{=}AsMe$	8.30	−194.4	−109.0	−31.9
$Me_2C{=}O$	9.71	−191.8	−92.4	−44.9
$Me_2C{=}S$	8.63	−198.1	−109.3	−33.4
$Me_2C{=}Se$	8.31	−197.1	−108.9	−33.3

Table 9. G4-Calculated Enthalpies Related to Enolization (in kcal/mol)

compound	step			
	to enol	A	B	C
$(CH_3)_2C{=}O$	11.5	103.7	−8.5	−83.7
$(CH_3)_2C{=}S$	3.6	101.9	−12.3	−86.0
$(CH_3)_2C{=}Se$	3.2	101.2	−23.9	−74.2
$(CH_3)_2C{=}NH$	4.2	101.3	−8.2	−88.9
$(CH_3)_2C{=}PH$	2.6	100.7	−22.6	−75.5
$(CH_3)_2C{=}AsH$	3.1	100.2	−27.9	−69.3

e. Keto–Enol Equilibria. It is well-known that the enol of acetone is about 12 ± 1 kcal/mol less stable than the ketone.[30] We calculated that the difference in energy is markedly reduced when O is replaced by S or Se.[1] An interest in seeing the effect of replacing =O with =NH, =PH, or =AsH led us to carry out the calculations summarized in Table 9. In this table, the second column gives the calculated enthalpies of enolization. It can be seen that acetone has a uniquely large enthalpy of enolization. This probably results from the large C=O bond energy, part of which is lost upon enolization. Even though the other enolization enthalpies are nearly the same, it might be possible to gain further information by examining the following purely hypothetical reactions for converting the carbonyl compound to the enol. The energies for steps A–C are also given in Table 9.



The first step involves cleavage of a C–H bond and is normally represented as a bond dissociation enthalpy. It is not much affected by the heteroatom. The second step is rotation of the CH_2 group to allow an interaction with the heteroatom. The enthalpy for this step is given in Table 9, and the heteroatom has a relatively large effect on this step, corresponding to the conjugation energy. The spin density at the heteroatom is of interest and was readily calculated using the Hirshfeld procedure,[21] which gave the following values: O, 0.260; S, 0.909; Se, 0.750; N, 0.381; P, 0.732; As, 0.795. There is a marked difference between O and NH versus the other heteroatoms.

The final step, C, corresponds to the bond dissociation energy of the enol, and the changes are similar to those found for the corresponding CH_3X–H bonds (Table 2). In most cases the changes cancel, leading to relatively constant enolization energies. However, with acetone, the A term is ~3 kcal/mol greater than for the other compounds and the B term has a small magnitude. Although iminoacetone also has a small B term, acetone has a smaller O−H BDE, giving it an overall ~8 kcal/mol greater enolization energy. The effects are mainly associated with the higher electronegativity of oxygen.

3. CALCULATIONS

All of the calculations were carried out using Gaussian 09.[31] The model chemistries used different theoretical levels for geometry optimization: CBS-QB3, B3LYP/6-311G(2d,d,p); CBS-APNO, QCISD/6-311G(d,p); G4, B3LYP/GTBas3; W1BD, B3LYP/cc-pVTZ+d.

4. CONCLUSIONS

In order to obtain further information on the differences between compounds containing O, S, or Se and the corresponding compounds containing NH, PH, or AsH, calculations of bond dissociation enthalpies, ionization potentials, enthalpies of reactions with protons, methyl cations, and lithium cations, and enolization enthalpies have been carried out. The calculations reproduced the available experimental data with high accuracy, allowing satisfactory predictions of the missing data. The four model chemistries gave essentially the same results, suggesting that the least computationally costly model should be of general use in studying organic compounds.

Among the heteroatoms studied in this report, O stands out as being different than the others, followed by N. The single- and double-bond dissociation enthalpies are largest with O, and it gives the largest ionization potentials, the smallest spin densities at the resulting radical centers, the least exothermic protonation energies, and the smallest degree of enolization. This appears to be largely a reflection of its higher electronegativity. The properties of the compounds with the other elements are fairly comparable.

The single- and double-bond dissociation enthalpies were found to be linearly related with a slope of about 2.5.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Calculated energies for bond dissociation energies, π-bond energies, ionization potentials, and reactions of $Me_2C{=}X$ and G4-derived Cartesian coordinates of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kenneth.wiberg@yale.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Computational resources used in this work were supported in part by the Yale University Faculty of Arts and Sciences High Performance Computing Center and by the National Science Foundation under Grant CNS-0821132, which partially funded the acquisition of the requisite computer facilities.

■ REFERENCES

(1) Wiberg, K. B.; Bailey, W. F.; Petersson, G. A. *J. Phys. Chem. A* **2011**, *115*, 12624−12630 and references therein.

(2) Wiberg, K. B.; Wang, Y.; Miller, S. J.; Puchlopek, A.; Bailey, W. F.; Fair, J. D. *J. Org. Chem.* **2009**, *74*, 3659−3664.

(3) Bailey, W. F.; Bartelson, A. L.; Wiberg, K. B. *J. Am. Chem. Soc.* **2012**, *134*, 3199−3207.

(4) Nyden, M. R.; Petersson, G. A. *J. Chem. Phys.* **1981**, *75*, 1843−1862.

(5) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **2007**, *126*, No. 084108.

(6) Petersson, G. A.; Tensfeldt, T. G.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1991**, *94*, 6091−6101.

(7) Martin, J. M. L.; de Olivera, G. *J. Chem. Phys.* **1999**, *111*, 1843−1856.

(8) Barnes, E. C.; Petersson, G. A.; Montgomery, J. A., Jr.; Frisch, M. J.; Martin, J. M. L. *J. Chem. Theory Comput.* **2009**, *5*, 2687−2693.

(9) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255−263.

(10) Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105−2109.

(11) Grev, R. S.; Schaefer, H. F., III; Baines, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 9458.

(12) Wiberg, K. B.; Nakaji, D. *J. Am. Chem. Soc.* **1993**, *115*, 10658−10664.

(13) Galbraith, J. M.; Blank, E.; Shaik, S.; Hiberty, P. C. *Chem.—Eur. J.* **2000**, *6*, 2425−2434.

(14) Chen, J.-X.; Kim, C. K.; Lee, H. W.; Xue, Y.; Kim, C. K. *J. Comput. Chem.* **2011**, *32*, 1361−1367.

(15) Chen, J.-X.; Kim, K. K.; Kim, C. K. *Bull. Korean Chem. Soc.* **2010**, *31*, 174−176.

(16) Wood, G. P. F; Radom, L.; Petersson, G. A.; Barnes, E. C.; Frisch, M. J.; Montgomery, J. A., Jr. *J. Chem. Phys.* **2006**, *125*, No. 094106.

(17) Levine, I. N. *Quantum Chemistry*, 2nd ed; Allyn and Bacon: New York, 1974; pp 261−266.

(18) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 614−615.

(19) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215−221.

(20) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37−40.

(21) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129−134.

(22) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217−5227.

(23) http://webbook.nist.gov/chemistry.

(24) Wiberg, K. B.; Schleyer, P. v. R.; Streitwieser, A. *Can. J. Chem.* **1996**, *74*, 892−900.

(25) Howard, S. T.; Foresman, J. P.; Edwards, P. G. *Can. J. Chem.* **1997**, *78*, 60−67.

(26) Martin, J. M. L.; Lee, T. J. *Chem. Phys. Lett.* **1996**, *258*, 136−143.

(27) Everett, D. H.; Wynne-Jones, W. F. K. *Proc. R. Soc. London* **1941**, *177A*, 499−516.

(28) Brown, H. C.; Fletcher, R. S. *J. Am. Chem. Soc.* **1949**, *71*, 1845−1854.

(29) Spitzer, R.; Pitzer, K. S. *J. Am. Chem. Soc.* **1948**, *70*, 1261−1264.

(30) Chiang, Y.; Kresge, A. J.; Schnepp, N. P. *J. Am. Chem. Soc.* **1989**, *111*, 3977−3980.

(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Isheda, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; *Gaussian 09*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2009.