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Carbon Dioxide Stability and C═O π-Bond Strengths

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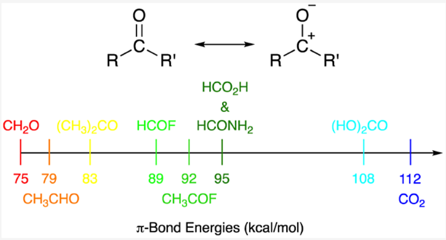
ABSTRACT: π-Bond energies for a series of C═O containing compounds including carbon dioxide are determined using G3 and W1 calculations. These two computational methods give results that are in good accord, and in the latter case span a 37 kcal mol^{-1} range from 75 (CH_2═O) to 112 (CO_2) kcal mol^{-1}. This sensitivity to substituent effects on the π-bond strength is attributed to Coulombic interactions between the oppositely charged carbon and oxygen atoms in the carbon−oxygen double bond. In contrast, carbon−carbon π-bond energies of a related series of compounds are found to be relatively constant (i.e., the variation is only 3 kcal mol^{-1}). The C═O π-bond strengths are also found to linearly correlate with the atomic charge at carbon as well as heats of hydration and hydrogenation.



INTRODUCTION

Plants, algae, and cyanobacteria use carbon dioxide and water to produce glucose by photosynthesis.[1] This remarkable transformation is the primary source of carbon for life on Earth even though CO_2 is relatively inert, and very stable with a heat of formation of −94.051 ± 0.031 kcal mol^{-1} (i.e., the difference in energy between CO_2 and the most stable forms of its constituent elements, dioxygen and graphite).[2] As a result large amounts of energy are produced upon formation of CO_2, and human activities exploiting this fact generate enormous amounts of this greenhouse gas (e.g., 37.2 billion metric tons were estimated to be produced from fossil fuels in 2022[3]). This is a cause for alarm and makes understanding the stability of CO_2 of considerable interest.

Resonance can be invoked to explain the stability of carbon dioxide since one of the lone pairs of electrons on either of the two oxygen atoms can interact with the other C═O π* orbital to afford a pair of dipolar resonance structures (Figure 1). This stabilizing feature has been referred to as a pair of 3-center 4-electron bonds and can be viewed as a type of anomeric effect.[4] Each oxygen atom serves simultaneously as an electron donor and acceptor, however, which makes it less clear how this leads to overall stabilization.[5] Group transfer reactions such as those illustrated in eqs 1 and 2, where one of the oxygen atoms in CO_2 is replaced by a better electron donor or acceptor (i.e., NH or S, respectively) are energetically unfavorable by 22.7 and 18.4 kcal mol^{-1}, respectively.[6] If one applies a correction for the differences in the CH_3O−H (105.3), CH_3NH−H (99.5) and CH_3S−H (87.0) bond dissociation energies (BDEs), then these reaction enthalpies would increase by 5.8 and 18.3 kcal mol^{-1}, respectively.[7] This suggests that an alternative explanation for the thermodynamic stability of CO_2 may be needed.

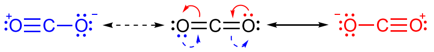


Figure 1. Resonance or anomeric stabilization of carbon dioxide.

$$CO_2 + CH_3NH_2 \rightarrow HNCO + CH_3OH \quad \Delta H^\circ_{rxn} = 22.7\ \text{kcal mol}^{-1} \tag{1}$$

$$CO_2 + CH_3SH \rightarrow COS + CH_3OH \quad \Delta H^\circ_{rxn} = 18.4\ \text{kcal mol}^{-1} \tag{2}$$

RESULTS AND DISCUSSION

Based upon Rablen's and Wiberg's work on electrostatic effects,[5,8,9] and the presence of two electronegative oxygen atoms in carbon dioxide, one might wonder if the two carbon−oxygen σ-bonds in CO_2 are unusually strong. There is no direct way to measure or compute this bond strength, so sequential transfers of a hydroxyl group from tetrahydroxymethane to methane were examined to probe the effect of multiple carbon−oxygen bonds at a single carbon atom center (eqs 3−6). High-level G3[10] and W1[11,12] computations were carried out to obtain the reaction enthalpies at 298 K, and as expected the two methods are in good accord so only the latter results are given in the text; the G3 energies are provided in the Supporting Information. These results are also analogous to Rablen's and Wiberg's findings for carbon tetrafluoride and tetramethoxymethane.[5,8,9] That is, each sequential group transfer of a hydroxyl group to methane is energetically unfavorable by

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approximately 20 kcal mol^{-1} (eqs 4−6) and the overall separation of all four hydroxyl groups is endothermic by 56 kcal mol^{-1} (eq 3).[13] In addition, the atomic polar tensor (APT)[14] charges at carbon are computed to increase monotonically upon replacing each carbon−hydrogen bond in methanol with a hydroxyl group. That is, the Hartree−Fock APT charges at carbon (q_C) with the hydrogen atom contributions summed into it are 0.34, 0.80, 1.20, and 1.65 in going from CH_3OH to $C(OH)_4$, respectively.[15,16] For the oxygens the charges are negative as expected for this electronegative atom and the average values span a narrow range from −0.34 (CH_3OH) to −0.40 ($CH_2(OH)_2$ and $CH(OH)_3$) and −0.41 ($C(OH)_4$). These results indicate that carbon−oxygen σ-bond strengths are strongly influenced by electrostatic effects and that substitution of each C−H bond in methanol with a OH group leads to a strengthening of the new C−OH bond and any already existing ones. This conclusion is supported by the W1 computed C−O bond strengths, which are as follows: 92.4 (CH_3OH), 99.2 ($CH_2(OH)_2$), 104.4 ($CH(OH)_3$), and 105.8 kcal mol^{-1} ($C(OH)_4$).

$$C(OH)_4 + 3CH_4 \rightarrow 4 \times CH_3OH \qquad \Delta H^\circ = 55.6\ \text{kcal mol}^{-1} \tag{3}$$

$$C(OH)_4 + CH_4 \rightarrow CH(OH)_3 + CH_3OH \qquad \Delta H^\circ = 20.2\ \text{kcal mol}^{-1} \tag{4}$$

$$CH(OH)_3 + CH_4 \rightarrow CH_2(OH)_2 + CH_3OH \qquad \Delta H^\circ = 20.0\ \text{kcal mol}^{-1} \tag{5}$$

$$CH_2(OH)_2 + CH_4 \rightarrow 2 \times CH_3OH \qquad \Delta H^\circ = 15.4\ \text{kcal mol}^{-1} \tag{6}$$

,

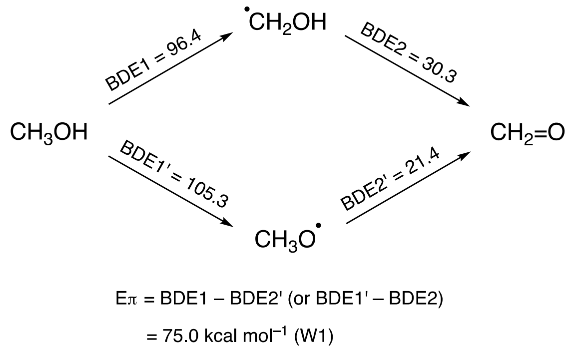
In addition to the two carbon−oxygen σ-bonds in carbon dioxide there are also two carbon−oxygen π-bonds. They may be unusually strong as well due to electrostatic interactions. To assess this possibility, the π-bond strengths of a series of carbonyl-containing compounds were computed using Benson's approach (Table 1).[17−19] In this method, the π-bond strength (E_π) of X═Y is defined as the difference in the H−X BDEs of H−XYH (BDE1) and H−XY$^\bullet$ (BDE2′) or, equivalently the difference between HXY−H (BDE1′) and $^\bullet$XY−H (BDE2). For formaldehyde (Scheme 1) this corresponds to the difference between the C−H BDEs for methanol and the methoxyl radical or the O−H BDEs for methanol and the hydroxymethyl radical. The resulting C═O π-bond strength is found to be 75.0 kcal mol^{-1}.[20,21]

Table 1. Experimental and Computed C═O π-Bond Energies and Carbonyl Carbon Atomic Polar Tensor (APT) Charges (q_C)

	E_π (kcal mol^{-1})		
cmpd	W1	expt[a]	q_C (APT)
CH_2═O	75.0	75.3 ± 0.1	0.68
CH_3CHO	79.1	79.3 ± 0.2	0.76
CH_3COCH_3	82.8	83.5 ± 0.4	0.89
$HCONH_2$	94.6		1.25
HCO_2H	94.6		1.31
HCOF	89.0		1.35
CH_3COF	91.8		1.36
$(HO)_2CO$	107.5		1.76
CO_2	111.9	110.0 ± 0.2	1.52

[a] Ref 19.

Scheme 1. Determination of the W1 Carbon−Oxygen π-Bond Strength in Formaldehyde, Where the Energies Are Given in kcal mol^{-1}



In a similar manner starting with formic acid one can derive a π-bond energy of 111.9 kcal mol^{-1} for CO_2 (see the Supporting Information for additional details). The 37 kcal mol^{-1} difference between the carbon−oxygen π-bond strengths for formaldehyde and carbon dioxide can be largely attributed to electrostatic interactions. Assuming this is the case, then one would also expect carbonic acid to have a similar C═O π-bond strength because it has four polar carbon−oxygen bonds as well. As anticipated, this is the case and the π-bond energy is 107.5 kcal mol^{-1}.[22]

To explore the relationship between C═O π-bond strengths and electrostatic stabilization further, a plot of the π-bond energies versus the carbon HF/6-31G(d) APT charges for all the compounds in Table 1 was examined (Figure 2). A reasonable correlation is obtained and a linear least-squares fit of the data affords E_π (kcal mol^{-1}) = 31.2 × q_C + 54.1, r^2 = 0.842; the analogous plot of the G3 data is given in the Supporting Information.[23−25]

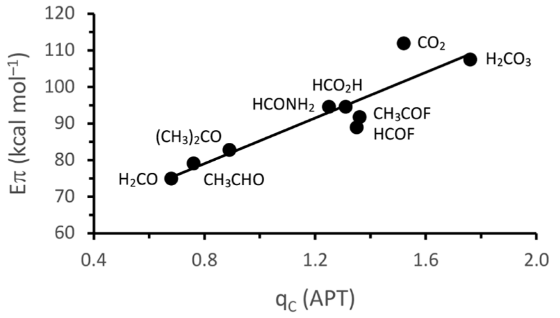
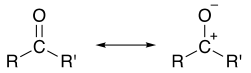


Figure 2. Plot of W1 π-bond energies vs HF/6-31G(d) APT charges at the carbonyl carbon.

The above results indicate that carbon−oxygen double bond strengths of carbonyl-containing compounds vary over a wide range in large part due to the Coulombic attraction between the positively charged carbon and negatively charged oxygen atoms. This is consistent with Wiberg's suggestion that carbonyl groups be written as two contributing resonance structures, one of which is covalent and the other a sacrificial form being dipolar in nature (Scheme 2).[8,26] This latter structure can account for the large dependence of E_π on the carbonyl substituents since

Scheme 2. Contributing Resonance Structures for Carbonyl-Containing Compounds.



charged sites typically are affected by substituents to a greater extent than neutral (noncharged) centers.

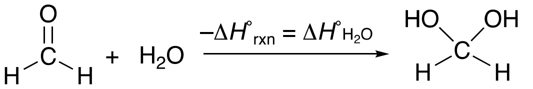
One would also expect due to this analysis that the variation in carbon−carbon double bond strengths should vary much less due to the presence of electronegative substituents such as OH or F because C═C bonds are relatively nonpolar. To test this prediction, π-bond strengths were computed for CH_2═CHX and CH_2═CX_2, where X = H, F, and OH (Table 2). As anticipated, the values only span a 3 kcal mol^{-1} range as opposed to 37 kcal mol^{-1} for the carbonyl compounds listed in Table 1.

Table 2. Experimental and Computed C═C π-Bond Energies

cmpd	E_π (kcal mol^{-1}) W1	E_π (kcal mol^{-1}) expt[a]
CH_2═CH_2	65.4	65.2 ± 0.1
CH_2═CHOH	65.1	66.2 ± 0.2
CH_2═CHF	67.0	
CH_2═$C(OH)_2$	68.4	
CH_2═CF_2	65.6	

[a] Ref 19.

Heats of hydration and hydrogenation ($\Delta H°_{H_2O}$ and $\Delta H°_{H_2}$, eqs 7 and 8) of formaldehyde, formic acid, carbonic acid, and



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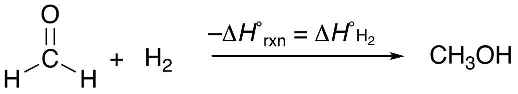

(8)

carbon dioxide were also examined (Table 3). These type of reactions in general are exothermic as written and thus heats of hydration and hydrogenation are positive numbers. In some cases, however, these transformations are endothermic and in these instances negative numbers are obtained. This is the case for the heats of hydration of HCO_2H, H_2CO_3, and CO_2 and the heats of hydrogenation for the latter two of these compounds. This is a reflection of their strong C−O π-bond energies and leads to correlations between E_π and q_C in both cases (Figure 3). It is also an additional indication of the importance of the Coulombic attraction in these species, and the unfavorable heats of hydration and hydrogenation of CO_2 are consistent with its remarkable stability.

Table 3. Computed Heats of Hydration and Hydrogenation Along with π-Bond Energies[a]

cmpd	$\Delta H°_{H_2O}$ W1	$\Delta H°_{H_2O}$ expt[b]	$\Delta H°_{H_2}$ W1	$\Delta H°_{H_2}$ expt[b]	E_π
CH_2═O	10.3	10.1	22.4	21.9	75.0
HCO_2H	−3.6		4.0	3.6	94.6
$(HO)_2CO$	−7.4		−0.1		107.5
CO_2	−6.8	−5.4	−3.3	−3.6	111.9

[a] All values in in kcal mol^{-1}. [b] Ref 19.

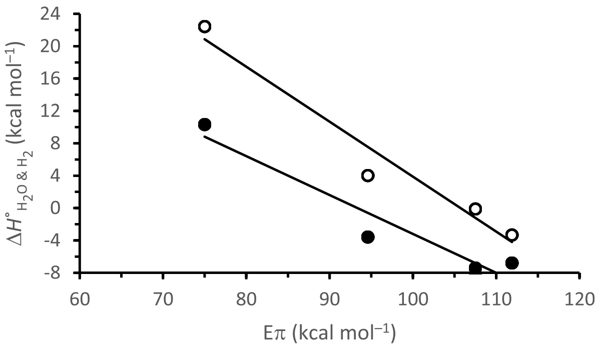

Figure 3. Plot of E_π versus $\Delta H°_{H_2O}$ (filled circles) and $\Delta H°_{H_2}$ (open circles) using W1 energies. Linear least-squares analyses afford: $\Delta H°_{H_2O} = -0.481 \times E_\pi + 44.9$, $r^2 = 0.922$ and $\Delta H°_{H_2} = -0.679 \times E_\pi + 71.8$, $r^2 = 0.957$.

■ CONCLUSIONS

Carbon dioxide is a remarkably stable compound with an unusually strong carbon−oxygen π-bond energy of 112 kcal mol^{-1} (which is larger than most σ-bonds) based upon W1 computations and Benson's method for determining π-bond strengths. This can be attributed to the large electronegativity of oxygen and the resulting Coulombic stabilization that arises from the attraction of the oppositely charged carbon and oxygen atoms. This cooperative electrostatic effect[5] also results in a broad range of carbon−oxygen π-bond strengths that span a 37 kcal mol^{-1} range depending upon whether X and/or Y = H, O, or OH in X(CO)Y. In contrast, analogous carbon−carbon π-bond energies only span a 3 kcal mol^{-1} range. Heats of hydration and hydrogenation were examined as well and were found to linearly correlate with C═O π-bond strengths.

■ COMPUTATIONS

Calculations were carried out on a MacIntosh computer and at the Minnesota Supercomputing Institute for Advanced Computational Research using the Gaussian 16 software package.[27] Starting structures were constructed using GaussView 6,[28] conformers were explored by carrying out B3LYP/cc-pVTZ+d[29,30] or HF/6-31G(d) optimizations, and then G3[10] and W1[11,12] calculations were carried out using the G3 and W1RO keywords. APT[14] charges with the hydrogen atom contributions summed into the heavy atoms were taken from the G3 computations and used throughout this work. Natural population analysis (NPA) and atoms in molecules (AIM) atomic charges were also computed and are provided in the Supporting Information.[16,24,25]

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its online Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.4c01024.

Computed structures, energies, charges, reaction enthalpies, force constants, and the complete citation to ref 27 (PDF)

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Notes

The author declares no competing financial interest.

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(19) The experimental values come from the Active Thermochemical Tables (ATcT, ref 6) which provide internally consistent and accurate thermochemical data based upon a combination of experiment and computed results

(20) An alternative approach for estimating π-bond energies is to use a compound's singlet−triplet(S−T) gap. For example, see: Uchimaru, T.; Tsuzuki, S.; Chen, L.; Mizukado, J. Computational Investigation of π-Bond Strengths in Fluorinated Ethylenes. *J. Fluorine Chem.* **2017**, *194*, 33−39.

(21) The computed G3 and W1 S−T gaps for $CH_2=O$ are 73.1 and 72.6 kcal mol^{-1}, which are in good accord with the values obtained using Benson's approach (i.e., BDE1 - BDE2').

(22) The G3 and W1 S−T gaps for CO_2 are 107.9 (G3) and 106.6 (W1) kcal mol^{-1} which are 4−5 kcal mol^{-1} smaller than the value obtained using Benson's method, but still indicates that the π-bond is exceptionally strong.

(23) A similar linear correlation is obtained if one uses NPA charges and an even better one is obtained using Bader's atoms in molecules (AIM) charges i.e., $E_\pi = 25.2\ q_C$ (AIM) + 52.5, $r^2 = 0.919$. The atomic charges and the latter plot are provided in the Supporting Information.

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